KINETIC THEORY
OF
GASES

Being a Text and Reference Book Whose Purpose Is to Combine the Classical Deductions with Recent Experimental Advances in a Convenient Form for Student and Investigator

BY

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FIRST EDITION
SECOND IMPRESSION

McGRAW-HILL BOOK COMPANY, INC.
NEW YORK: 370 SEVENTH AVENUE
LONDON: 6 & 8 BOUVERIE ST.; E. C. 4
1927

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PRINTED IN THE UNITED STATES OF AMERICA

THE MAPLE PRESS COMPANY, YORK, PA.

TO MY TEACHERS:

ROBERT ANDREWS MILLIKAN

AND

EXUM PERCIVAL LEWIS

TO WHOM THE INSPIRATION FOR THIS
BOOK IS LARGELY DUE

PREFACE

The last thirty years have seen the beginning and development of a new period in physics and chemistry, namely the atomic period. In contrast to the period preceding it where nature's processes were described in terms of continua, recent developments have emphasized the discrete structure of the submicroscopic universe. Thus, today one hears of the atoms of matter, the atoms of electricity, and even the atoms of energy, the quanta. Accordingly the modern physical sciences are demanding and constantly using atomic terminology, concepts, and methods of analysis. It is therefore important that the physicist and chemist have available a fairly complete understanding of these methods.

Of all atomic concepts, the atomic theory of matter is the oldest and perhaps the most complete. In particular because of its relative simplicity the problems of the atomic nature of gases, in the form of the kinetic theory of gases has attained the highest degree of perfection in this field. Its admirable methods of analysis are therefore indispensible not only for prospective physicists, but for both chemists and physicists engaged in experimental or teaching work.

When attempting to teach a course on the kinetic theory of gases, at the University of Chicago, in the summer of 1922, the writer discovered that there was in print but one text in the English language on modern kinetic theory. This text was far beyond the scope of the average American college student including even the first-year graduate students. The lack of facility in foreign languages among the students precluded references to texts in foreign languages. Finally, in his own field of work, which depends on the kinetic theory, the writer and his students have been much hampered by lack of a handy reference book containing a collection of the classical and more modern aspects of the kinetic theory. This book was written in an attempt to meet this situation.

The purpose of this book is, therefore, to furnish a modern text and reference book on the kinetic theory of gases for student,

teacher, and investigator in chemistry and physics. The scope of the book is to present as concisely as possible the various kinetic theory concepts and classical derivations for use by students who are beginning their third year of college work and on to the more advanced students and investigators who wish a handy reference describing more elaborately the phenomena in question. It should furnish a useful preparation to the more advanced texts and monographs on the subject including those dealing with statistical mechanics. It endeavors to develop the various concepts as independently of preceding concepts as possible, so as to avoid references to earlier chapters. Besides a simple introduction of each concept it gives derivations of three types, to wit: elementary ones, using little or no calculus; more advanced classical derivations; and in some cases the most recent developments available. It also contains the comparison of the theoretical deductions with modern experiment and a critique of the theories. Where possible the experimental methods are briefly outlined. It has the added feature of including a complete chapter giving a summary and discussion of the kinetic theory of low-pressure phenomena. A complete theoretical summary of this sort, to the writer's knowledge, has so far not been published. Finally, it contains the application of the kinetic theory methods to two more or less recent fields of research, that of dielectric and magnetic phenomena in gases and of gaseous ionisation.

The writer wishes particularly to acknowledge his indebtedness to his colleague Dr. Edward Condon at whose instigation this book was undertaken. Dr. Condon originally intended to be a collaborator in this work. Lack of time prevented his doing so. The writer is indebted to him for the preparation of a large part of Chap. II, of the first two thirds of Chap. III, of the collection of the material for Chap. VI, and for some of the developments therein contained. In fact a large portion of the discussion of experimental results in parts 2 and 3 of Chap. VI are due to Dr. Condon's efforts.

The writer's thanks are also due to the following authors whose kindness and courtesy permitted him to use developments of some of the theories used in their texts. They are: Prof. P. Debye whose admirable treatment of dielectric and magnetic phenomena in gases in Vol. VI "Theory of Electric and Magnetic Molecular Properties" of Marx's "Handbuch der Radiologie"

rnished most of the material for Chap. X; Prof. Clemens haefer from whose splendid book "Einfuhrung in die Theoret- che Physik" the concise treatment of the Boltzmann derivation the Maxwell distribution law (Chap. IV), and the derivation of an der Waals' equation from the theorem of the Virial (Chap.) were taken; Prof. E. Bloch for permission to translate the nall section of his book "Theorie Cinetique des Gaz" dealing th the proof of the Maxwell distribution law from the width of ectral lines. In this connection the courtesy of Messrs. ethuen and Company of London must be mentioned for per- itting the purchase from them of the rights to make a anslation.

The writer also desires to acknowledge the assistance and formation he obtained in setting up some of the derivations and finding useful references, to Prof. G. Jaeger for his admirable esentation of the kinetic theory in the section of Wincklemann's Iandbuch der Physik, Vol. III," and to Prof. K. Jellineck for e valuable material and references found in his "Lehrbuch der ıysikalischen Chemie," including the treatment of the problem evaporation of liquids given in Chap. IX. The latter book is veritable gold mine of information and is notable for the com- steness of the bibliography.

Finally, the writer desires to express his appreciation to Miss lma Hutchings without whose patient help in the preparation the manuscript the book would have been impossible.

LEONARD B. LOEB.

BERKELEY, CALIF.,
February, 1927.

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INTRODUCTION

Scarcely thirty years ago, before the discovery of X-rays, rapid progress in physics had come to a standstill and the physicist surveyed a world in which was presented a pretty clearly defined system of nature, which could be depicted in terms of classical mechanical analogies, although the knowledge in all its details was not complete. With the discovery of Röntgen, there followed a period of feverish experimentation in which the sole aim was to gain new facts about the manifold phenomena surrounding the electron and the atom. In this search little attention was paid to a careful coordination of the new discoveries with the fundamental system of mechanics of Newton and of the times just preceding 1895.

It was about twenty-five years ago (1900) that it began to dawn on the physicists that, after all, the beautiful mechanical explanations which had stimulated so many researches, and had seemed so satisfying, were not infallible, and that such analogies too closely drawn as to the mechanism of radiation, and as to the structure of the ether, were, in fact, wrong. Today physicists seem to have come to the point of realizing that many of the observed phenomena cannot be included in the mechanical concepts of thirty years ago without a complete modification of those concepts. Such a picture as stable non-radiating electron orbits in the atom, a picture which one is inevitably forced to accept in order to correlate many of the phenomena, appears to vitiate the electrodynamics of yesterday. It is possible that a mechanism may yet be found by which such a condition is brought about, and thus the mechanical analogies may be saved—partially at least. At present, however, the trend seems to be away from all attempts at "explanation" and towards the formulation of the observed phenomena in terms of a consistent system of

relations, the correctness of which depends on being based on a few fundamental experimentally verified axioms and the proper mathematical manipulations of the equations derived from these axioms. Such formulations are seen today admirably presented in the theory of relativity and in the so-called "quantum theory." From them, given a particular situation, it is possible to predict quantitatively and definitely what phenomena will be observed in certain fields. It is thus possible to coordinate, predict, and perhaps control the phenomena by these means, but they cannot be "explained." Possibly it will in the end be the ultimate aim of science thus merely to describe, and in a measure coordinate, the physical phenomena. Perhaps the notion of the "explanation" is a mental immaturity of the past decades of science, just as the ultimate "why" which was abandoned in science in bygone years was a still greater immaturity that the human mind had to outgrow.

Be that as it may, let it for the present be assumed that the notion of the necessity of the "explanation" is an immaturity of mind. It will then be much the most satisfying mode of procedure for immature but developing (*i.e.*, growing) minds. In the world of physics there are today two types of such growing minds—those of the students who are just discovering the ideas of the last decades (and mentally living through the experiences of Joule, of Clausius, of Maxwell, and of Boltzmann), and that of the investigator baffled and puzzled by some new phenomenon. Both these types of mind have to struggle in unknown territory, both have to grasp new relations and new notions, and to both the simple expedient of concrete mechanical visualization is the most obvious course of procedure. With more maturity in the study of physics, or with a clear understanding of the new phenomenon as it is visualized, the more complete and correct formulation in some general scheme of nature may become possible, may even necessary, because of the failure of the mechanical analogy in its details. At any rate, in the process of achieving this ultimate goal, that inspiring and stimulating method of mechanical visualization will have played its rôle. It is thus of value to the growing mind to be familiar with this mode of procedure, and in no domain of physics has the mechanical visualization had such a sweeping success as in that field termed the kinetic theory of gases. In fact, it is today perhaps the only field of physics in which the mechanical picture has not been dimmed

by the breakdown of our mechanical concepts. True it is that here and there the kinetic theory of gases borders on the peculiar mysteries of the quantum relationships, and truer it also is that the kinetic-theory concepts must constantly be modified to meet details or new discoveries. Yet today the theory stands as perhaps one of the most beautiful and satisfying pictures of physical behavior, and the analysis of new phenomena by means of its fundamental and perhaps crude concepts is now in various domains leading to valuable experimental results. So it is hoped that the student of this book will receive the same stimulus and enthusiasm from its study which inspired the writer when some years ago, as a student, he entered the field of physical research, under its spell.

Before proceeding to a consideration of the text a word of explanation will perhaps not be out of place. For the sake of simplicity, and for the purpose of appealing to the imagination of the beginning student, the agreement of the simple relations deduced with experiment and the accuracy of some of the laws cited may appear to be exaggerated. A careful scrutiny of the book as a whole should show that great care has been taken to avoid any *real misconception* without, however, killing the enthusiasm engendered by failing to emphasize a successful agreement. It must be realized that the writer is thoroughly aware of the deficiencies of the kinetic theory, although he is its ardent advocate. He regards the advance of scientific discovery and its correlating mechanical theory as a series of approximations to the true sequence of phenomena. What, for example, was a great triumph of yesterday in accounting for the coefficient of viscosity of a gas by an expression $\eta = \frac{1}{3} Nm\bar{c}^2$ is today, on the kinetic theory but a crude approximation which neglects the present view of molecules whose apparent average diameter determined by intermolecular force fields is necessarily a function of their average velocity. Doubtless in years to come the successful and beautiful treatment by Chapman will, in its turn, be but a second-order approximation to an even more complicated and more precise series of relationships. Such improvements are, nevertheless, continual advances rather than revolutionary changes. Thus, imperfect as the theory may be today, it is an advance over previous concepts and for practical purposes may be of incalculable value. It is the endeavor in this book to

avoid confusing the student at the outset with a statement of all the complexities encountered in more modern work. Accordingly, the theory will be logically developed from the simplest conceptions. As, with increasing knowledge of the facts, the discrepancies begin to appear to the student, the weaknesses of the theory will be carefully pointed out. Then in later chapters, when the mind is ready for them, detailed descriptions of the difficulties and of the way in which the theory attempts to meet them will be given. It is felt that in *this way only* can the best aims of the student be served. The reader is, therefore, warned that before he accept a simple assertion as the complete, accurate, and final statement of a law he would do well to consult the index for references to a more complete discussion in a later and more appropriate chapter. In some cases the attention of the reader will be specifically called to such discussions in the text. With this caution the reader may open the book and discover for himself the fascinating romance of the eternal motions of the myriads of minute solar systems called molecules which constitute that state of matter which is termed the gaseous state.

CHAPTER I

HISTORICAL*

Age of Philosophical Speculation.—Nearly 2300 years ago (400 B.C.) the Greek philosophers Leucippus, Democritus, and their pupils pictured a world made out of minute particles or atoms which were in constant motion. Later (95 B.C.), Lucretius,[1] who was familiar with the earlier writings, pictured gases somewhat as they are pictured today.† However true these philosophic speculations may seem today, they were then no more than wild guesses. Many another philosopher of that time fitted gases into his scheme of nature in a very different manner. As these pictures were not in accord with later discovery, they were ignored and forgotten. It is, then, because the fortunate coincidence that a speculation made 2300 years ago happens to agree with an experimental fact of today that a group of persons frequently assert that there is nothing new in the world, and that the more modern atomic theory was discovered by the Greeks. This, of course, is absurd.

Birth of an Hypothesis.—The kinetic theory of gases could not have been legitimately propounded as a theory with any semblance of reality until the nature of heat was known, and until the relationship of heat to work and energy had been established.[2] During the period 1760 to 1800 the views of Black[3] the advocate of the caloric theory of heat, still held the scientific stage, whence they had evolved from the first measurements on quantity of heat. From then on until 1850 the famous experiments of Rumford and Joule[3] on the relation between heat and work were in progress, so that by 1856 the time was ripe for the two independent papers of Krönig and of R. Clausius (1857), in which

* Throughout this book numbered references are to references at the close of each chapter.

† The famous poem *"De Naturæ Rerum,"* in which this scheme is propounded, is well worth reading. It appears in Everyman's edition. In reading it, it is to be noticed that the scheme of nature devised is a logical deduction based on certain crudely observed phenomenon, such as the conservation of matter. (Book I, lines 146–328.)

the kinetic theory of gases was proposed and based on an experimental footing.

Before these two definite enunciations of the theory there had been earlier attempts, none of which were complete enough to be included with them. In fact, Clausius admits to having been familiar with a paper of Joule's published in 1851, in which Joule computed the gas pressure on the basis of the heat motions of the gas molecules. There was an article of a similar nature by a practically unknown physicist Herapath, in 1821. Credit must also be given to the mathematical physicist and genius Daniel Bernouilli, for in his then little known "Hydrodynamics," published in 1738, he had built up a correct and very complete kinetic theory of gases. He had at that time no experimental basis for his assumptions, and accordingly his theory must be classed among the philosophic speculations.

Establishment of an Hypothesis.—The deductions of Clausius were of sufficient accuracy and completeness so that his paper attracted widespread attention, and such master minds as Maxwell[4] and Kelvin were stimulated to interest themselves in the theory from 1860 to 1880. In later years Boltzmann,[5] O. E. Meyer,[6] Jaeger,[7] Jeans,[8] Knudsen,[9] Chapman, Enskog, Sutherland,[18] and others have also contributed a considerable amount. The theory as it was left by Maxwell, Kelvin, and Boltzmann, however, remained no more than an hypothesis, for, in spite of many quantitative agreements between the theory and the behavior of gases, no proof of the separate existence of the atoms and molecules had been obtained, nor had any observations been made that could really demonstrate the continual heat motions of the molecules.[10] This left the kinetic theory a very successful and interesting analogy, but that was all.

Retarded Development. School of Energetics.—From 1890 to 1908 the theory suffered a retarded development due to the violent attacks on it by Wilhelm Ostwald and his school of "Energetics."[11,12,13] This was at a period when thermodynamics had been found to be a very useful tool of the physicist and chemist. At that time, perhaps somewhat as with Relativity today, the physicists sought to solve all the problems of the universe by thermodynamics. Now thermodynamical reasoning does not require a knowledge of the precise mechanism of a reaction for its applications. All that is required is a complete knowledge of the energy and heat relations of a cycle of opera-

tions. Ostwald, accordingly, argued that with the thermodynamical treatment of a process one knew all that there was essential to be known about the process and that further mechanical assumptions as to the mechanism of the reactions were gratuitous hypotheses. He was correct in asserting that the mechanical assumptions of the kinetic theory were unproved hypotheses. He was, however, wrong in urging that the rather sterile thermodynamical reasoning be substituted for the neat and stimulating analysis of the kinetic theory, for, strangely enough, science progresses chiefly by the mechanical analogies of nature's processes which occur to the mind of the investigator. And the kinetic theory is just such a mechanical analogy. In fact, it seems to be the very fallibility of such mechanical pictures which makes experimental test imperative and hence leads to further investigations and clearer knowledge. Science cannot progress much through the manipulations of equations indicating only the heat and energy transfers in a reaction, for such manipulations do not generally suggest further experiments.

Birth of a Theory.—Fortunately, these attacks were brought to an abrupt end through the brilliant experiments of Jean Perrin[14] in France in 1908. Perrin succeeded in quantitatively demonstrating the existence of the continual heat motions of the molecules of a liquid by a study of the Brownian movements of suspended particles. These proofs, as will later be seen, were of such a definite nature that even Ostwald accepted them and relinquished his exclusive claims for "energetics." Recently, these results have been extended to gases with a far higher degree of accuracy through the beautiful oil-drop experiments of R. A. Millikan.[15]

New Advances.—The final developments in the kinetic theory of gases, upon which the closing chapters have not yet been written, were due to the new methods of study opened up by the discovery of X-rays in 1895. The X-rays led to a study of the carriers of electricity in gases, the ions and electrons.[16] Now it has been shown that the ions are charged molecules or groups of molecules of the gases, and the electrons act as essentially mathematical point charges from the point of view of the kinetic theory.[16,17] Their electrical charges enable the ions and electrons to be singled out from the other molecules, and thus permit their properties to be studied after encountering the other gas molecules under varying circumstances. The result is that the

kinetic theory of gases has made much progress in the able hands of Langevin and Lenard, J. J. Thomson, Franck, Townsend, and Compton,[19] through the additions which have come to it from the theory of the gaseous ions.

Today, then, the kinetic theory of gases can be regarded as being far beyond the speculative philosophy of the Greeks, and far beyond the kinetic hypothesis of Clausius and Maxwell. In fact, it is as well-established a theory (that is, a close working mechanical analogy to the real processes) as any theory which is accepted by science.

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17. See Chap. XI, Sec. 104.
18. For work of Chapman, Enskog, and Sutherland see Chap. VI, Secs. 62, 64, and 69.
19. For references to this work see all of Chap. XI.

Books Recommended

a. For historical outline of the development of the concepts of heat, Mach: *loc. cit.*
b. Lucretius: *Loc. cit.*
c. Historical Sketch and the Introduction to Jeans' "Dynamical Theory of Gases," *Cambridge Press* 1911.

CHAPTER II

THE MECHANICAL PICTURE OF A PERFECT GAS

1. The Mechanical Equivalent and the Kinetic Hypothesis. In the historical outline it was stated that there could be no proper justification of the kinetic-theory hypothesis until the relation between heat and work had been established. It is now necessary to show why this was so. It will be seen that it was not strange that Joule, one of the first to establish the relation between mechanical work and heat, should also have been one of the first to try to formulate a kinetic theory of gases.

When a gas like helium is heated in an enclosed vessel so that it cannot expand, two things occur: first, it absorbs a given quantity of heat per unit mass, and, second, its temperature rises. This heat is stored in the gas in some form and is given out again on cooling. Furthermore, in absorbing the heat there is no appreciable change in the gas except the increase in temperature and an increase in pressure. This pressure increase in the gas is what would cause the gas to expand and do work corresponding, in the ideal case, to the heat put in. The question then arises as to how the gas can absorb heat and increase its pressure.

Assistance is derived in understanding this phenomenon by inquiring into the meaning of temperature, and as to how the temperature is related to the pressure. The experiments of Boyle, in 1662, showed that for a given temperature the relation between pressure and volume of a gas was given by the relation $pv =$ constant, where p is the pressure and v the volume. Later, Charles, Mariotte, and Gay-Lussac studied the behavior of gases at constant volume and constant pressure as the temperature was increased. It was found that at constant volume an increase in temperature of $\Theta°$ gave a change in pressure represented by the equation

$$p = p_o(1 + A\Theta),$$

in which p is the pressure at the temperature Θ and p_o is the pressure at 0° on the thermometric scale used. If v_o is the constant volume of the gas, the equation may also be written as

$$pv_o = p_ov_o(1 + A\Theta).$$

In virtue of Boyle's law, the left-hand side of the equation is constant and will remain the same even if v_o be changed to some new value v. Hence it is possible to write

$$pv = p_o v_o(1 + A\Theta).$$

If to p on the left-hand side the value p_o be assigned, the expression

$$v = v_o(1 + A\Theta), \text{ readily follows.}$$

This is the law for the change of volume with temperature which was discovered experimentally. Experimentally, it does not hold accurately for any gases, for the constant A in the pressure equation differs from that in the volume equation (see Secs. 48 and 51). It is approached more accurately by the gases that are furthest from their condensation temperature. For such gases the A is nearly the same and the condition in which this is so can be called the limiting state to which all gases strive the farther they are removed from their condensation temperatures. Strictly, it is only a limiting case, and a gas obeying this law is defined as an ideal gas. Elementary treatments of the kinetic theory which will be derived in this chapter deal with such gases.

If it be assumed that both equations hold and that A is the same for pressure and volume changes, one can proceed to use the common equation

$$pv = p_o v_o(1 + A\Theta).$$

Factoring A out of the parenthesis, the equation becomes

$$pv = p_o v_o A\left(\frac{1}{A} + \Theta\right).$$

This equation gives a new insight into the process of expansion, for if $\Theta = -1/A$, $pv = 0$, that is, at $-1/A$ either p, v, or both are 0. Since Θ is a temperature, $1/A$ is a temperature, and it is the temperature which, if attained below the zero from which Θ is measured, would make pv equal to zero. Thus, since A is a universal constant for the expansion of an ideal gas, $-1/A$ gives a new definition of zero on an absolute scale. That is, $(1/A)°$ below the zero from which Θ is measured is the absolute zero of temperature at which a gas exerts no pressure. On this basis $1/A + \Theta$ may be replaced by T, calling T the *absolute temperature*. If the constant quantity $p_o v_o A = R$, be written with the understanding that v_o corresponds to the volume of 1 gram-molecule of the gas, the *equation of state* for an ideal or perfect gas is given by

$$pv = RT.$$

This equation will at once aid in understanding the nature of temperature.* Its interpretation is aided by means of dimensional analysis of the left-hand side of the equation. Pressure is the ratio of a force to an area, that is, it is a force divided by the square of length. Volume is the cube of a length. The product pv has thus the dimensions of a force times a length. But, dimensionally, force times a distance represents work done or energy.† Thus RT is dimensionally a work or an energy, and as T increases the product RT increases in proportion, and hence the energy that is represented by pv in the gas increases. That is, RT is proportional to an energy that goes into the gas as it is heated, and T is a measure of this energy. When T is 0 then the energy is 0. Now for constant volume p is also increased in proportion to the increase in energy and the key to an interpretation of the

* A moment's reflection shows that temperature is entirely different from the other measurable quantities of physics. The important stages in the development of the concept of temperature cannot be overemphasized.

The notion of temperature has its origin in our sense perception of warmth and coldness. The sensations of an individual are far too relative and crude to serve as a working basis for temperature measurements, and so physical means have been developed for the purpose, which are independent of the thermal perceptions of the observer. These are based usually upon the recognition by the observer of changes in some property of a substance, known as the thermometric substance, which is placed in the space of which the temperature is desired to be known (*e.g.*, the expansion of liquids, etc. which give a purely empirical scale).

The utility of the temperature concept in physics is twofold. In the first place, the assignment of numbers representing the temperatures of a set of bodies makes it possible to determine in what direction heat will flow between the bodies if any of them are placed in thermal contact. This use is embodied in the statement that heat flows from bodies of higher to bodies of lower temperature. Obviously, however, for this purpose any scale of temperature suffices so long as larger numbers are always assigned to warmer bodies. The other functions of the temperature concept are developed in the study of thermodynamics and are concerned with the rôle played by temperature in conditioning the efficiency of all processes which are designed to transform heat into mechanical work.

It is this second property of temperature which serves to define the absolute temperature scale. Rigorously, the absolute temperature scale is to be regarded as derived from the second law of thermodynamics. The justification for the approach to the subject given in the preceding paragraph lies in its historical correctness, and, further, in the fact that the perfect gas thermometer is the actual experimental mode of establishing the absolute temperature scale.

† Force times distance may also represent a torque, but as this does not enter into considerations such as these it need not be discussed here.

phenomenon lies in *finding a mechanism* by which both the pressure of the gas and its internal energy are simultaneously increased in proportion.

This was solved by Joule by the assumption that a gas was made up of molecules, or particles in constant motion. Such particles striking a solid wall and rebounding from it elastically will transfer momentum to it. The rate of momentum transfer to the wall gives the force exerted by the particles on the wall and represents the pressure. If the pressure be calculated, as will be done in Sec. 5, it will be seen that it depends in a simple way on the kinetic energy of the gas molecules. Thus the energy represented by the quantity RT is related to the kinetic energy of motion of the molecules, while the pressure is also a consequence of this. This picture requires, however, that a simple relation exists between heat and mechanical energy or work. The idea underlying this concept is that, in a gas, heat is nothing else than the kinetic or mechanical energy of motion of the gas molecules, so that, in expanding, a gas does work at the expense of the kinetic energy of its molecules, which represent its heat energy.

The assumptions made by Joule, of the molecular nature of the gas, and which form one phase of this picture, were not as novel at the time as might be gathered from this discussion, for as will be seen in Sec. 8, the molecular nature of a gas had been pretty well foreshadowed by Avogadro in attempting to account for the laws of chemical combination of gases. Thus, the contribution of Joule lay in associating the heat taken up by the gas with the increase in kinetic energy of its molecules, and showing that this also gave the required pressure change. With such an introduction it is possible to proceed to set forth a group of assumptions about the molecules and their motions which will enable further analysis to be carried on. As will be seen, these assumptions apply to an ideal gas. They do not conform to reality. They, however, sufficiently simplify the problem to make it possible to proceed with an elementary analysis. As the understanding of the processes advances, it will become possible to alter the simple assumptions to conform to the real gases.

2. The Numerical Value of RT.—It is worth while before proceeding further to obtain a numerical value for R, the universal gas constant. This may be calculated as follows: A gram-molecule of gas at 0°C. and 760 mm of Hg (1 atmosphere of

pressure) occupies a volume of 22,410 cm³.* The value of A, evaluated with respect to 0°C., is given by experiment as 0.003665 Since by the above R is given as

$$R = p_0 v_0 A,$$

then $R = 1 \times 22{,}410 \times 0.003665$ cm³ atmospheres per degree
$= 82.07$ cm³ atmospheres per degree.

The cm³ atmosphere is a rather awkward unit of energy. More common ones are the absolute C.G.S. unit, the erg, or the classical heat unit, the calorie. Making use of the density of mercury and the value of gravity the relation follows:

$$1 \text{ atmosphere} = 1{,}013{,}300 \text{ dynes per sq. cm.}$$

Choosing as the definition of the calorie the amount of heat required to raise 1 gram of water from 15 to 16°, the value of the mechanical equivalent of heat is

$$1 \text{ cal.} = 4.182 \times 10^7 \text{ ergs.}$$

In view of these results the value of R can be given in mechanical or in heat units as follows:

$$\begin{aligned} R &= 82.07 \times 1.0133 \times 10^6 \text{ cm}^3\text{-dynes per cm}^2 \text{ per degree} \\ &= 8.316 \times 10^7 \text{ ergs per degree} \\ &= 1.988 \text{ cal. per degree.} \end{aligned}$$

3. The Model of a Perfect Gas. In order to carry on the analysis, the following simplified picture of a gas must be made. The gas is to be considered as an assemblage of particles called molecules which move freely in the space occupied by the gas, colliding with each other and with the walls of the vessel. The assumptions upon which the mechanical picture of a gas is founded, and which are introduced in this chapter and elaborated and modified in the following chapters may be enumerated as follows:

1. A gas consists of particles called molecules which in a stable state and in a given type of gas are all alike. The mass of the molecules will be denoted by m.

2. The molecules are in motion, and as they are material bodies Newton's laws of motion may presumably be applied.

3. The molecules behave as elastic spheres of diameter σ. In perfect gases the number of molecules in the space considered is small enough so that the mean distance between the molecules

* The conditions denoted here of 0°C. and 760 mm of Hg will be designated at N.T.P. hereafter, meaning Normal Temperature and Pressure.

is large compared to their diameter, and thus for these elementary considerations the space they occupy may be disregarded.

4. In perfect gases no appreciable forces of attraction or repulsion are exerted by the molecules on each other or on the substance of the containing vessel.

(1) The reasons for the assumption of the molecular nature of the gas have been introduced in Sec. 1. The assumptions of the stable state and similarity of the molecules are introduced to simplify the initial calculations.

(2) That the molecules are endowed with motions follows from the fact that they are assumed to have kinetic energies of agitation and are reflected from the walls, producing pressure. That they obey Newton's laws is a consequence of the assumption that they are material bodies in motion, and Newton's laws are assumed applicable to all material bodies.

(3) The assumption of perfect elasticity is necessary in order to account for the reversibility of the absorption and emission of heat. It is an essential assumption if the correct relation between heat and work is to be maintained for the ideal gas, for if it be assumed that they are not elastic, kinetic energy gained on heating would go into the deformation of the atoms when inelastic impacts took place. Unless this energy could be given back on cooling, heat would be lost on heating and cooling, or if the kinetic energy were converted into work after heating, less work would be obtained than was put in and the relation between heat and work would not be fulfilled. Actually, in some gases that are chemically reactive, like Cl_2 and Br_2, this elasticity does not hold and energy goes to atomic deformation, which may be radiated away as electromagnetic radiation, as is shown in Chap. IX. In general, the assumption of elastic impacts is, however, justified. The assumption of point molecules is a simplifying assumption which corresponds to reality only as a rough approximation. The consequence of the finite size of the molecules is seen in Chap. III.

(4) Gravitational forces do undoubtedly act between the molecules. These forces are exceedingly minute. The force of gravitation between two bodies of equal mass m is given by $f = G\frac{m^2}{r^2}$, where r is the distance between them and G is the constant of gravitation. This force f is $6.658 \times 10^{-8}\ m^2/r^2$ dynes, if m be in grams and r in cm. Since m is of the order of 10^{-24} grams

for the H_2 molecules and r is of the order of 10^{-8} cm when the molecules are in contact, the force is minute indeed. A better idea can be gained of the influence of these forces if the kinetic energy of the molecules at 0°C. is compared, which by Sec. 11 is about 5×10^{-14} ergs, with the gravitational potential at contact between molecules, which is of the order of $6 \times 10^{[illegible]} \times 10^{[illegible]} \cdot 10^{[illegible]}$ or 10^{-48} ergs for two H_2 molecules. The *intermolecular forces of attraction* are, however, much greater and their potential energies at molecular contact become comparable to the kinetic energies of agitation near the condensation temperatures. For ideal or perfect gases they may for simplicity be neglected. Their influence, however, is measured for real gases by the term a/v^2 in the Van der Waals' equation studied in Chap. V.

4. Molecular Motions.—Preparatory to their use in later developments a statement of Newton's laws of motion will here be given. These are fundamental to the classical mechanics on which the kinetic theory is based:

1. A body continues in its state of rest, or of straight uniform motion, except in so far as it is compelled to alter that state by impressed force.

2. Change of motion is proportional to the impressed motive force, and takes place in the direction in which that force is impressed.

3. Reaction is always equal and opposite to action, that is, the mutual actions of two bodies are always equal and take place in opposite directions.

The statement of the laws is included here mainly for reference purposes. Mathematically, the position of a particle is determined relative to a Cartesian coordinate system by its coordinates x, y, z, which give its position at the time t. The velocity components are then dx/dt, dy/dt, and dz/dt and the momentum is defined as having the components $m\,dx/dt$, $m\,dy/dt$, $m\,dz/dt$. As the components of the force are F_x, F_y, F_z, the second law yields the equations

$$F_x = \frac{d}{dt}\left(m\frac{dx}{dt}\right);\quad F_y = \frac{d}{dt}\left(m\frac{dy}{dt}\right);\quad F_z = \frac{d}{dt}\left(m\frac{dz}{dt}\right).$$

The kinetic theory has frequently to deal with assumed perfectly elastic collisions between individual molecules and between a molecule and a wall. The study of elastic collisions as governed by Newton's laws of motion is greatly facilitated by the use of

two principles, which are mathematical consequences of Newton's laws, the conservation of kinetic energy and of momentum in the collision. In an elastic collision:

1. The sum of the kinetic energies of the colliding bodies before impact is equal to the sum after impact.

2. The sum of the momenta of the two bodies before impact is equal to the sum after impact.

A simple application of these principles, the result of which will be needed later, is to the case of the elastic impact of a spherical ball striking a wall at normal incidence. Let m, v_1, v_2 be the mass and initial and final velocities of the ball, and M, V_1, V_2 these same quantities for the wall. Then

$$\frac{1}{2}mv_1^2 + \frac{1}{2}MV_1^2 = \frac{1}{2}mv_2^2 + \frac{1}{2}MV_2^2$$

and $$mv_1 + MV_1 = mv_2 + MV_2,$$

so that $$m(v_2^2 - v_1^2) = M(V_2^2 - V_1^2).$$

dividing these by, $$m(v_2 - v_1) = M(V_2 - V_1),$$

$$v_2 + v_1 = V_2 + V_1.$$

If the wall be immovable, then $V_2 + V_1 = 0$, so that

$$v_2 = -v_1,$$

i.e., the ball rebounds with the same velocity as that with which it struck the wall. The total change of momentum of the ball is $2mv$, where v is now the common velocity before and after impact. This is also the impulse communicated to the wall.

5. The Kinetic Interpretation of Gas Pressure.—In this section will be given an extremely simple mechanical deduction

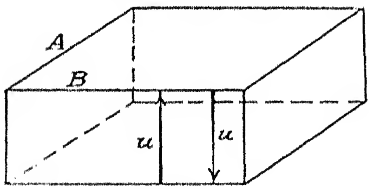

FIG. 1.

of the equation of state, substantially as it was first given by Joule in 1851.

The ν molecules of the gas are contained in a rectangular box of edges A, B, and C (Fig. 1). It is supposed that there is no actual streaming, or body motion, of the gas, the motions of the molecules being perfectly chaotic. Let u be the mean speed of the molecules, and for simplicity's sake let it be supposed that they

all move at the same speed. Owing to the random nature of the motions it may be supposed that the motions are equivalent to a situation in which one-third of the molecules are moving parallel to the length, one-third parallel to the breadth, and one-third parallel to the depth of the box.*

Every time a molecule collides with a wall its direction of motion will be reversed (Sec. 4), and so its change of momentum will be $2mu$. In 1 second a molecule which is traveling parallel to an edge of length C will traverse the length of the vessel u/C times, and so will collide with each of the end walls $u/2C$ times per second. As one-third of the molecules are moving this way, the number of collisions per second on an end wall is $u\nu/6C$, where ν is the number of molecules in ABC. Thus the total change of molecular momentum per second by an end wall of area AB is

$$2mu \times \frac{u\nu}{6C} = \frac{\nu mu^2}{3C}.$$

But by the second law of motion this rate of change of momentum of the molecules is equal to the total force exerted upon them. By the third law this is also the force which they exert on the wall. The pressure on the wall is equal to this force divided by the area, so that

$$p = \frac{1}{3}\frac{\nu mu^2}{ABC}$$

or

$$pv = \frac{1}{3}\nu mu^2 = \frac{2}{3}\left(\frac{1}{2}\nu mu^2\right) = \frac{2}{3}E.$$

This equation makes it evident that the value of pv is simply two-thirds of the total kinetic energy E of the molecules. Comparison with the equation of state shows how the temperature of the gas is simply proportional to the total kinetic energy of the molecules of the gas.

6. Work of Compressing a Gas.—An instructive picture of the way in which mechanical work done on a gas is transformed into

* This apparently natural assumption is one which has a very great significance in the kinetic theory, as will be seen in Sec. 91 of Chap. IX. It assumes that if the molecules are great in number and have random motions the velocities and hence kinetic energies are equally distributed among the three degrees of freedom of motion along the three coordinate axes. It is, in fact, an application of the *theorem of equipartition of energy* to the degrees of freedom of motion in gas, to be discussed in Chap. IX.

thermal energy of the molecules is obtained by a simple extension of the analysis of the preceding section.

The experimental fact to be explained is that a gas is warmed when it is compressed adiabatically (*i.e.*, without loss of heat through the walls of the container) and, conversely, is cooled when it expands adiabatically.

Suppose the gas to be contained in a cylinder which is equipped with a piston which moves without friction in the cylinder. If A is the area of the piston, then pA will be the force which the gas will exert tending to drive the piston outward. Hence pA is also the force which must be exerted by some external agency to maintain the piston in equilibrium. If a greater force be exerted by this external agency, the piston will move inward, or if a lesser force be exerted, it will move outward.

It is interesting to consider the effect on the molecular motions of steadily pushing the piston in at a speed of α cm/sec. It will be supposed that this speed is small compared to the molecular motions, so that no actual streaming of the gas is set up. If C is the length of the cylinder the number of collisions per second on the moving piston will be $u\nu/6C$ as before. But now the molecules are striking a moving wall and the effect is different from that of the preceding section on this account.

The simplest way to see the effect of the piston's motion is the following: Consider how a collision of a molecule with the wall would appear to a person riding along with the piston. The molecule approaches him with a speed $u + \alpha$ and leaves him with the same speed after the collision with the wall. But to leave the piston with a speed $u + \alpha$ relative to it means to move relatively to the cylinder with a speed $u + 2\alpha$.

The change in kinetic energy at each collision is an increase of amount:

$$\frac{1}{2}m(u + 2\alpha)^2 - \frac{1}{2}mu^2 = 2mu\alpha + 2m\alpha^2 = 2mu\alpha\left(1 + \frac{\alpha}{u}\right).$$

Since by hypothesis α/u is small, it may be neglected. Multiplying by the number of collisions per second, an expression is obtained for the amount of kinetic energy imparted to the molecules by the piston in a second:

$$\frac{1}{3}\frac{m\nu u^2}{C}\alpha = \frac{p\nu}{C}\alpha = pA\alpha.$$

In a small time dt piston will move a distance αdt and the volume of the gas will be changed by $dv = A\alpha dt$. In this time the energy imparted to the molecules will be

$$pA\alpha dt = pdv.$$

It is thus seen that when a gas is compressed adiabatically by a *slowly moving* piston the work done goes into increasing the energy of the molecular motions, the amount of work thus done being simply equal to the product of the pressure which the gas would exert on a stationary piston at each successive position by the change in volume. It is evident that all that has been said applies equally well when the piston is moved slowly outward—in this case the molecules communicate energy to the wall at the same rate pdv, and the gas is thereby cooled.

7. Irreversible Compression.—Students of thermodynamics are already familiar with the important distinction in that subject between reversible and irreversible processes. Reversible processes, such as the reversible compression or expansion of a gas, must be carried out in such a way that the forces are in equilibrium at all stages of the process and as a result all the motions occur with infinite slowness. If the processes be irreversible, it is shown in thermodynamics that there is always an attendant degradation of energy from the "perfectly available" mechanical energy to the thermal energy of "limited availability."

The discussion of adiabatic compression of a gas, given in Sec. 6, admits of an illuminating extension to show the mechanical picture of the distinction between reversible and irreversible processes. In considering the communication of energy to the walls by the molecules, it was supposed that α was so small that α/u was negligible. This is the case in the infinitely slow reversible processes. If α/u is not negligible, then it is evident that the accurate expression for the energy exchange between the piston and the molecules in time dt is

$$\frac{1}{3}\frac{m\nu u^2\alpha}{C}\left(1 + \frac{\alpha}{u}\right)dt.$$

If P is the pressure exerted by the gas against the *moving* piston, then in time dt the force PA will have acted through the distance αdt so the work done by the piston will be

$$PA\alpha dt = Pdv.$$

Returning to the accurate expression for energy exchange, this may be written as

$$\frac{pv}{C}\alpha\left(1 + \frac{\alpha}{u}\right)dt = p\left(1 + \frac{\alpha}{u}\right)dv$$

as the amount of energy communicated to the molecules in the volume change dv. Equating the two expressions in virtue of the law of conservation of energy and dividing by dv:

$$P = p\left(1 + \frac{\alpha}{u}\right).$$

This indicates that the *actual pressure P which a gas exerts when it is being compressed is greater than the statical pressure p which it would exert against a stationary wall at the corresponding stages of the compression.* Similarly, *during expansion (α is negative) the actual pressure P is less than the statical pressure p.*

The obvious result of these conclusions is that if a gas be compressed at a finite velocity and then expanded to its original volume, all of the work of compression will not be regained on expansion and so the gas will be left warmer than it originally was. Thus the simple kinetic picture clearly portrays a conclusion gained in thermodynamics by rather abstruse reasoning.

8. Avogadro's Rule.—In Secs. 1 and 2 the experimental fact that R has the same numerical value for all gases when a mol (*i.e.*, a gram molecule) of the gas is considered has already been presented. This important result calls for more extended discussion.

The concept of molecular weight as used thus far is a conclusion derived originally from the quantitative experimental laws of chemical combination. After Lavoisier, in 1774, had enunciated the law of conservation of mass in chemical reactions the next great step was the formulation by Richter and Proust of the law of definite proportions: *A definite chemical compound always contains the same elements united in the same proportion by weight.*

It was then possible to ascertain the relative combining weights of the various chemical elements. Thus if the combining weight of hydrogen were taken as unity, experiment showed that the combining weights of chlorine, oxygen, and sulphur were 35.5, 8, and 16 respectively. On the basis of the atomic theory these numbers mean, respectively, the weights of the atoms of chlorine, oxygen, and sulphur which combine with one atom of hydrogen when the weight of the hydrogen atom is taken as the unit. But it is important to notice that we are not entitled to conclude from these data alone that these numbers represent the relative weights respectively, of single atoms of chlorine, oxygen, or sulphur.

This will be true only in case a single atom of these elements enters into combination with hydrogen in the compound from which the combining weights were determined.

This work was followed by the publication in 1808 by John Dalton of the *law of multiple proportions*, which says that: *When two elements unite in more than one proportion, for a fixed mass of one element the masses of the other element bear to each other a simple ratio.* Dalton further gave a brilliant explanation of these laws on the basis of his atomic theory as presented in his work, "A New System of Chemical Philosophy." In the same year Gay Lussac generalized the results of his experiments into the statement of another important law: *When gases combine they do so in simple ratios by volume, and the volume of the gaseous product bears a simple ratio to the volumes of the reacting gases when measured under like conditions of temperature and pressure.*

Dalton did not understand the applicability of Gay-Lussac's discoveries to his atomic theory and so questioned their correctness. The Swedish chemist Berzelius was the first to see the importance of the volume law, and by making the hypothesis that equal volumes of gases under like conditions of temperature and pressure contain equal numbers of *atoms* he made considerable progress in systematizing the chemical data.

But there was one great stumbling block which Berzelius could not pass. Experiment showed that *two* volumes of hydrochloric acid were formed from the combination of *one* volume of hydrogen and *one* volume of chlorine. On Berzelius' view this would mean that *two "atoms"* of hydrochloric acid result from the combination of *one* atom of hydrogen with *one* of chlorine. In other words, the indivisible atoms must have been divided by the reaction.

Although his views were not widely known or accepted until many years later, the way out of this difficulty was made plain by the Italian physicist Avogadro, in 1811. He achieved this simply by introducing the distinction between the *atoms* and the *molecules* of a substance. The molecule of a compound like hydrochloric acid was regarded from the first as being made up of the atoms of the elements of the substances from which it was formed. It was then a natural step to suppose that the units of structure in an elementary (*i.e.*, one which is not a compound) gas were also molecules containing two or more atoms of the elements. This view, due to Avogadro, explains at once Berzelius' difficulty. Thus, if it is supposed that the molecules of hydrogen

and chlorine each contain two atoms, the volume relations come out just right.

The hypothesis of Avogadro may, then, be stated as follows: *Under the same conditions of temperature and pressure, equal volumes of different gases contain the same number of molecules.*

From the experimental point of view the hypothesis is now an established fact. The experimental results in support of it may be briefly enumerated as follows:

1. The complete coordination of the structural formulae of thousands of chemical compounds.

2. Correspondence between positive-ray and mass-spectrograph measurements of atomic weights with those obtained from vapor-density measurements.[1]

3. Results as to the masses of hydrogen and oxygen atoms obtained by Blackett at Cambridge from the study of forked α-particle trails.[2]

4. Concordant values obtained for the number of molecules in a gram-molecule from widely different experimental methods, such as those of Brownian movements and measurement of the charge on an electron.[3]

9. Equipartition of Energy.—The experimental verification of Avogadro's hypothesis, together with the simple kinetic picture presented in the foregoing, now point to an extremely interesting conclusion. This is that the mean kinetic energy of the molecules of all gases is the same at equal temperatures.

Consider a mol of gas A and a mol of gas B in separate containers at the same temperature. Then since the value of R is the same for all gases,

$$RT = P_A V_A = P_B V_B.$$

By Sec. 5 this leads to

$$\frac{1}{3}N_A M_A u_A{}^2 = \frac{1}{3}N_B M_B u_B{}^2.$$

Since by Avogadro's rule $N_A = N_B$ it follows that

$$\frac{1}{2}M_A u_A{}^2 = \frac{1}{2}M_B u_B{}^2.$$

Had the gases been ideal and were they in the same volume at the same time, the conditions would have been unaltered and the equations deduced above would be applicable. Hence the conclusion *that the mean kinetic energy of the molecules in the two*

gases is the same. This conclusion is a statement, in a limited form, of the principle of equipartition of energy one of the most important principles of the kinetic theory of gases, concerning which more will be said later.

It is to be noticed that in arriving at the equipartition of energy use was made of the *experimental fact* of Avogadro's rule and the *theoretical equation* relating the product pv to the mean kinetic energy of the molecules. If the kinetic theory is to be fully developed as a set of logical deductions from the assumptions given in Sec. 3 it is evidently necessary that all conclusions be obtained on an entirely theoretical basis. From the discussion just given it is seen that if Avogadro's rule were derived theoretically, assuming equipartition, then the theory would be in perfect and independent accord with experiment. The theoretical deduction of the rule is one of the important mathematical triumphs of the kinetic theory which will be discussed in detail later. The theory as usually presented proceeds, it will be interesting to observe, in the opposite order from that pointed out by experimental developments, in that the equipartition of energy is given theoretical discussion, and from this Avogadro's rule is derived instead of conversely.

10. The Law of Partial Pressures.—John Dalton, pioneer student of atomic theory, discovered the experimental law governing the pressure exerted by a mixture of several gases which do not react chemically. The results of his investigations in this field may be stated as follows: *The total pressure exerted by the mixture is equal to the sum of the pressures which the several gases would separately exert if each were to occupy the vessel alone.*

In developing the kinetic-theory view of this law it is to be supposed that the molecules of different kinds exert no forces on each other, other than the elastic forces introduced by collisions. Then on making a mixture of gases no kinetic energy will be gained or lost provided the impacts are perfectly elastic as previously assumed, so that the total kinetic energy will be equal to the sum of the kinetic energies of the gases put into the mixture.

In accordance with the simple theory given, the total pressure exerted by the mixture P will be related to the total kinetic energy E by the equation

$$P = \frac{2}{3}\frac{E}{v},$$

where v is the volume. On the other hand, the partial pressures or pressures which each gas would exert if it alone filled the space are given by equations of the same form

$$p_1 = \frac{2}{3}\frac{E_1}{v}; \quad p_2 = \frac{2}{3}\frac{E_2}{v}; \quad p_3 = \frac{2}{3}\frac{E_3}{v}; \text{ etc.,}$$

so that, since

$$E = E_1 + E_2 + E_3 + \ . \ . \ . \ ,$$

it follows that

$$P = P_1 + P_2 + P_3 + \ . \ . \ . \ ,$$

which is nothing other than Dalton's law of partial pressures.

11. Molecular Speeds.—The results which have been obtained already allow the calculation of the mean speed of the molecules. From Sec. 6

$$pv = \frac{1}{3}\nu m u^2.$$

Now νm is the total mass of the gas, so on dividing by v and writing ρ for the density of the gas the result is:

$$p = \frac{1}{3}\rho u^2$$

$$u = \sqrt{\frac{3p}{\rho}}.$$

The density and the pressure of a gas are quantities which are known experimentally and so u may be computed. Thus at 1 atmosphere pressure and at 0°C. the density of nitrogen is 0.00125 gram per cc. Atmospheric pressure is $760 \times 13.6 \times 980$ dynes per sq. cm, so substitution in the formula yields

$$u = 4.93 \times 10^4 \text{ cm per sec.}$$

Another way of arriving at this result shows the relation between the molecular speed, the molecular weight, and the temperature. Combining the empirical equation of state with the theoretical equation,

$$RT = \frac{1}{3}N_A m u^2$$

$$u^2 = \frac{3RT}{N_A m} = \frac{3RT}{M},$$

where M is the molecular weight of the gas in grams, R applies to a mol, and N_A is the number of molecules in a mol.

In the deductions of this chapter, it may again be emphasized that all of the molecules were regarded as having the same speed. It will be seen later (Sec. 27) that this is not actually the

case, and that when a gas is held at constant temperature and pressure the molecular speeds are distributed about their mean value in such a way that most of them are very close to the mean, but a few are very small and a few are very great. The speed which has just been calculated for the molecules is the speed which each of the molecules must have in order that the total kinetic energy be the same as that actually possessed by the gas.

Such a speed is a kind of mean speed which is different from the ordinary arithmetic mean of the actual speeds of the individual molecules. Let $v_1, v_2, v_3, \ldots v_\nu$ be the actual speeds of each molecule at any instant, then the arithmetic mean of the speeds would be simply

$$\bar{v} = \frac{1}{\nu}(v_1 + v_2 + v_3 + \ldots + v_\nu).$$

On the other hand, if u is the single speed which makes the total kinetic energy the same as the actual kinetic energy,

$$\frac{1}{2}\nu m u^2 = \frac{1}{2}m\,(v_1^2 + v_2^2 + v_3^2 + \ldots + v_\nu^2)$$

or

$$u^2 = \frac{1}{\nu}(v_1^2 + v_2^2 + v_3^2 + \ldots + v_\nu^2).$$

From this it is evident that u is the square root of the arithmetic mean of the squares of the velocities. It will hereafter be referred to simply as the root-mean-square speed. Numerically, it is very nearly the same as the average speed $\bar{c}$, as will be shown after the distribution of molecular speeds has been studied.

The molecular velocities are thus seen to be extremely great compared with the velocities of ordinary every day experience. The velocity of the projectile fired by the 75-mile range cannon used against Paris in the World War was 1.7×10^5 cm/sec. The speed at which a projectile would have to be fired vertically upward in order to be able to free itself from the earth's attraction (the so-called "velocity of escape") is 1.1×10^6 cm/sec. The velocity of escape from the moon is 2.4×10^5 cm/sec. Since $RT = pv = \frac{1}{3}N_A mu^2$, $\frac{1}{2}mu^2 = \frac{3}{2}\frac{RT}{N_A}$. Here N_A is the number of molecules in a gram-mole. Hence $\frac{1}{2}mu^2 = 5.62 \times 10^{-14}$ ergs at 273° abs. (0°C.) if $N_A = 6.06 \times 10^{23}$, the accepted value. This is the molecular kinetic energy at 0°C. Another speed with which the molecular speeds may be compared is that of

the velocity of sound waves in the same gas. In elementary treatises on sound waves it is shown that this velocity v depends on the pressure and density in the following way:

$$v = \sqrt{\frac{\gamma p}{\rho}},$$

in which γ is the ratio of the specific heat at constant pressure to the specific heat at constant volume. For perfect monatomic gases it will be seen later that it is a consequence of the kinetic theory, also borne out by experience, that $\gamma = 5/3$, so that

$$\frac{v}{u} = \sqrt{\frac{\gamma}{3}} = \frac{1}{3}\sqrt{5} = 0.7452,$$

which leads to the interesting conclusion that the velocity of sound in a perfect monatomic gas is approximately three-fourths of the mean speed of the molecules in that gas.

Since the theory requires such enormous speeds for the molecules, the natural inquiry is, why it is that the molecules are not observed (by their direct effects) to travel so rapidly? Thus, at first sight, it might seem that a little hydrogen released in one corner of a large room should be observed in other parts of the room a fraction of a second later.[4] This seeming contradiction was raised against the kinetic theory in its earliest days as a serious difficulty. The answer lies in the evaluation of the enormous number of the molecules in a cubic centimeter. It is thus obvious that the number of collisions experienced by a molecule in a short time will be enormous. Each collision deflects the molecule from its straightforward course; in fact, it may reverse the direction of its motion; so it is easy to see the answer to the seeming contradiction of theory and experience.

The proper development of an explanation for the slowness of diffusion of gases and other related matters opens up a whole division of kinetic theory—that which deals with the concept of the mean free path of the molecules. Discussion of this will be reserved for the next chapter. Now, however, the results of the further developments may be anticipated by the statement that the average distance between molecular collisions will be found to be about 10^{-5} cm under usual gas pressures.

12. Exercises.—1. Compute the root-mean-square speed of the molecules at 298°K, of H_2, He, N_2, Hg vapor, and of a gas made up wholly of electrons, taking the mass of the electron as $1/1840$ times that of the H atom.

2. Show, from the theory of this chapter, that the Avogadro number (*i.e.*, number of molecules in a mol of substance) and the mass of the individ-

ual molecules are related to known data in such a way that if either of them were determined experimentally the other would be known.

3. Assuming the Avogadro number to be 6.08×10^{23}, compute the mass in grams of a hydrogen molecule.

4. The velocity of escape from a spherical body of mass M and radius r (using the earth's mass and radius as units) may be worked out simply from the principle that the escaping particle must initially possess an amount of kinetic energy which is equal to the difference between the potential energy of the particle at infinity and at the surface of the body. Derive the relation and:

a. Compute the temperature at which the root-mean-square speed of hydrogen molecules is just equal to the velocity of escape from the earth.

b. Compare the mean speed of mercury vapor molecules at 5000 K. with the velocity of escape from the sun.

5. When a gale of 60 miles an hour is blowing, are all of the air molecules moving with the wind at a given instant? If not, what is the average backward speed in miles per hour of molecules which are moving in a direction opposite to that of the wind? Assume $T = 298$ K.

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CHAPTER III

THE MEAN FREE PATH—CLAUSIUS' DEDUCTIONS

13. Concept of Free Path.—Continuing the development of the mechanical model of a gas, begun in the last chapter, it is now of importance to consider the question, How far do the molecules travel, on the average, between their successive collisions with each other and with the wall? At the end of Chap. II it was foreshadowed that the answer to this question would make clear the slowness of gaseous diffusion in the face of the great molecular speeds.[10] It will also be seen that the heat conductivity and the viscosity of gases are intimately tied up with the question of the mean free path.

In the preceding developments, the molecules of a gas have been regarded as perfectly elastic spheres whose diameters were vanishingly small compared to the mean distance apart of the molecules. The gas molecules were thought of as moving with a velocity u such that the total kinetic energy of the translatory motion was the same as the total kinetic energy of the actual translatory motions (Sec. 11). As the molecules exert no forces on each other except during collision, their paths between collisions will be rectilinear and described at constant speed. At certain times in the life history of a molecule it may happen that the molecule will go a comparatively great distance between successive collisions, at others two successive collisions will come very close together. In other words, the distances traveled between successive collisions, *i.e.*, the free paths, will be widely different, but will be distributed around a certain mean value. This mean distance traveled by a molecule between successive collisions is defined as the mean free path.

Kinetic theory owes this very fruitful concept to Clausius,[9] who opened up a whole new branch of investigation by its introduction. He was led to these considerations by the very difficulty which has already been noted—that of the slow diffusion of gases.

Let n be the average number of collisions experienced by a molecule in a second, then $1/n$ is the average time between collisions, and if the mean speed be u cm/sec., the mean free path L in cm will be given by

$$L = \frac{u}{n}.$$

The evaluation of the mean free path is thereby made to depend upon the calculation of the average number of collisions which a molecule experiences in a second. This is the mode of approach to the problem originally adopted by Clausius. The deduction of this number, following the argument of Clausius, will now be given.

14. Number of Collisions.—Let the diameter* of the molecules be denoted by σ and consider a gas comprised of ν molecules occupying a container of volume V and of surface Σ. Actuated by their thermal motions, the molecules will be moving about in a random manner, as often in one direction as in another, with the mean speed u. For simplicity, the molecules will all be supposed to have the same speed, as in preceding arguments.

When a molecule collides with the wall its center comes to a distance of $\frac{1}{2}\sigma$ from the wall. When a molecule collides with another molecule the minimum distance between the centers of the two molecules will be σ. If, then, the attention be fixed on one particular molecule, it is seen that there are certain regions of the containing vessel which cannot be occupied by the center of this particular molecule. For convenience, call the center of this molecule A. Then A certainly cannot be within a distance of $\frac{1}{2}\sigma$ from the wall, nor can it lie within any sphere described about the center of any of the molecules with a radius equal to the diameter of the molecules.

It is thus seen that the collisions experienced by the molecule A may be discussed by considering the collisions of the point A its center, with the surface S, which bounds the regions in which A can lie. In other words, the question of the collisions of spherical molecules with other such molecules or with the walls may

* For the discussion of the meaning of σ the student is referred to Sec. 19 and Secs. 49, and 52 in Chap. V.

be replaced by the equivalent problem of the collisions of a point with a surface.

The surface S may be better visualized by considering how an instantaneous picture of the molecules would look. It would find each molecule situated at a certain point within the volume V (Fig. 2). Surrounding each molecule would be a sphere of radius σ, these spheres constituting part of the discontinuous surface of exclusion S, the remaining part of S being a surface parallel to the walls of the vessel but distant $\frac{1}{2}\sigma$ from them. The point A might, then, with equal likelihood, occupy one part of the space within this surface as another. The volume available to A will be denoted by U.

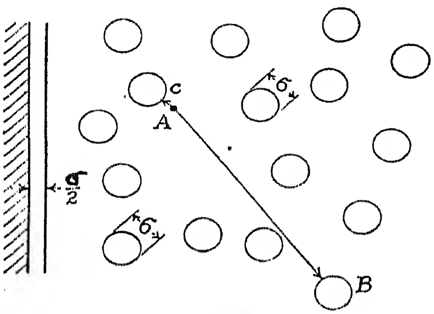

Fig. 2.

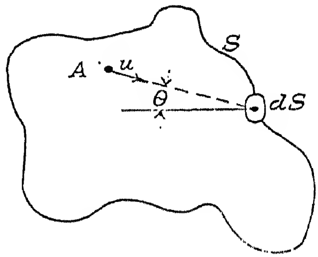

Fig. 3.

But all of the equally likely positions of A are not associated with equal probability of collision with the surface S. Consider an element dS of the surface S toward which the molecule is moving in such a direction that its path makes an angle θ with the normal to dS (Fig. 3). The chance that the molecule will strike dS in the time dt depends on the relative motion of the molecule and this portion of S. Regarding the molecule as stationary, the element dS will move toward A with a speed u sweeping out a volume

$$u \cdot dt \cdot dS \cdot \cos\,\theta.$$

If at the time t the point A is anywhere within this volume, it will collide with dS during the time t and $t + dt$. As all positions of the molecule are equally likely, the probability P_{dtds} of a collision with dS in time dt may be written:

$$P_{\theta\,.\,dtds} = \frac{u \cdot \cos\,\theta}{U} \cdot dt \cdot dS.$$

This expression depends on the angle of approach of A toward dS. This element may be eliminated by averaging over all of the equally probable directions of approach. Take the normal to dS as the axis of polar coordinates. The probability P of A approaching dS in a direction contained between θ and $\theta + d\theta$ will be proportional to the solid angle at dS subtended by these directions. This element of solid angle is measured by the area on a sphere (Fig. 4) of unit radius of the circular zone between the angle θ and $\theta + d\theta$ and so is equal to

$$2\pi \cdot \sin\theta \cdot d\,\theta.$$

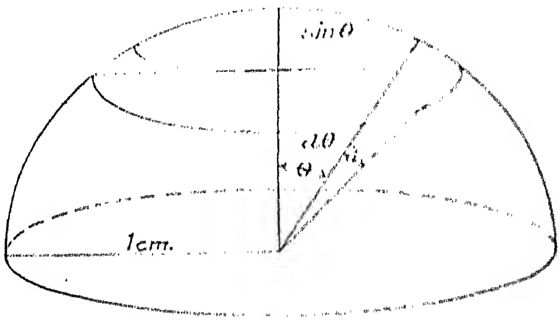

FIG. 4.

The total solid angle about a point is 4π, so the chance that θ lies between θ and $\theta + d\theta$ is

$$\frac{2\pi \sin\theta d\theta}{4\pi} = \frac{\sin\theta d\theta}{2}.$$

But it is evident that a collision of A with dS is possible only when $\theta < \frac{\pi}{2}$, so that the chance of collision of A with dS in time dt, in a form independent of θ, is

$$P_{dtdS} = \frac{u}{2U}\int_0^{\frac{\pi}{2}} \cos\theta \sin\theta \cdot d\theta dt dS = \frac{u}{4U} \cdot dt \cdot dS.$$

As this chance is independent of the particular part of S under consideration, it may be integrated at once over the whole surface:

$$P_{Sdt} = \frac{uS}{4U} \cdot dt$$

The expression on the right is then the probability that A will collide with any part of the surface S in the time dt. The greater this time interval, the greater is the likelihood of a collision. As

the probability does not depend on the particular instant chosen, dt may be replaced by a finite time interval Δt. Choose Δt so that the probability $P_{S\Delta t}$ is equal to unity, *i.e.*, certainty of a single collision. The proper value of Δt is, evidently,

$$\Delta t = \frac{4U}{uS}.$$

Supposing that the amount of time consumed in a collision is negligible, the number of collisions in unit time is then

$$n_1 = \frac{1}{\Delta t} = \frac{uS}{4U}.$$

15. The Quantities S and U.—In the expression just found for the number of collisions in unit time, the quantity S is the total area of the surface on which A, the center of a particular molecule, might collide. It is made up of two parts: (1) the total area of the spheres drawn about all the other molecules with a radius equal to the diameter of the molecules, and (2) the total area of a surface which is generated as the locus of a point which is at all times distant $\frac{1}{2}\sigma$ from the walls of the containing vessel. The first term is simply equal to $4\pi(\nu - 1)\sigma^2$, and since in all cases ν, the number of molecules in V, is enormously great compared to unity, this may be taken as $4\pi\nu\sigma^2$. The second term is quite negligible in comparison with the first in most cases, so that in all cases the much smaller difference between it and Σ, the total area of the walls of the containing vessel, may be ignored. This fact can readily be seen from the following calculation: The surface area of a sphere of radius 1 cm is 4π cm^2. The volume is $\frac{4}{3}\pi$ cm^3. This contains, at N.T.P., 2.7×10^{19} molecules per cm^3, each of radius about 1×10^{-8} cm, and of radii of spheres of exclusion of 2×10^{-8} cm. The surface of each sphere is $16\pi \times 10^{-16}$. The total area of the molecules in this volume is $\frac{4}{3}16\pi^2 \times 2.7 \times 10^3$ cm^2, or 5.7×10^5 cm^2. This is 4.5×10^4 times as great as the surface of the spherical vessel with the molecules in it.

The quantity U, it will be remembered, is the total volume available to the point A. It is evidently somewhat less than the total volume of the containing vessel V. Let the difference be denoted by b, so that

$$U = V - b.$$

This difference b may, like S, be naturally regarded as the sum of two parts: (1) the volume from which A is excluded by virtue of the presence of the other molecules, and (2) the volume of the region within $\frac{1}{2}\sigma$ of the walls of the container. Further consideration of the value of b will be undertaken later (Sec. 19).

16. Approximate Free Path.—Introducing the expressions for U and S in the formula for the mean number of collisions per second of a given molecule,

$$n_1 = \frac{u \cdot (\Sigma + 4\pi\nu\sigma^2)}{4(V - b)}.$$

The relation $L = u/n$ between number of collisions and free path then gives the free-path formula:

$$L = \frac{4(V - b)}{\Sigma + 4\pi\nu\sigma^2}.$$

In many cases, the quantity b is negligibly small in comparison with V, and Σ is also negligible in comparison with $4\pi\nu\sigma^2$ (see end Sec. 15). By Sec. 19 b is $\frac{2}{3}\pi\sigma^3N$. That is, b for molecules of σ 2×10^{-8} cm for a cm³ of gas at N.T.P. is $\frac{16}{3}\pi \times 10^{-24} \times 2.71 \times 10^{19}$ cm³, or 4.5×10^{-4} cm³, while V is 1 cm³. Another way of getting at this is by considering the volume of a given mass of water compared to that occupied by the same mass of steam or water vapor. Eighteen grams of water occupy, roughly, 18 cm³. In the gaseous state 18 grams of water would occupy 22,410 cm³ of volume. Moreover, in the aqueous state the volume occupied by the water molecules is still greater than b. Dropping Σ and b from the expression, the free-path formula simplifies into:

$$L = \frac{V}{\pi\nu\sigma^2}.$$

Denoting by $N = \nu/V$, the number of molecules per cm³ of the gas, *i.e.*, the molecular density, the formula may be written

$$L = \frac{1}{\pi N\sigma^2}.$$

It is obvious from this expression that the mean distance between molecular impacts is dependent only on the molecular diameter σ and the number of molecules per cm³. This formula makes it evident that *the mean free path is inversely proportional to the molecular density.* Since for equal volumes and temperatures the

pressure exerted by a perfect gas is known to be proportional to the molecular density, the important result follows that *the mean free path is inversely proportional to the pressure.*

Elementary Deduction.—A simple deduction of the expression for the mean free path may be made as follows: Assume all the other molecules at rest and one molecule moving with a velocity u. If the center of any other molecule comes within σ cm from the first they will collide (Fig. 5). Thus, as the moving molecules moves u cm in 1 sec., there will be a volume $\pi\sigma^2 u$ which contains all the molecules with which it collided. If there were N molecules per cm³ in the volume, that means that the moving molecule in going u cm in the gas in 1 sec. collided with $\pi N\sigma^2 u$ molecules. The average distance gone between collisions L is, therefore, u, the distance traversed, divided by $\pi N\sigma^2 u$, the number of impacts experienced. Thus $L = u/(\pi\sigma^2 Nu)$ or $L = 1/(\pi\sigma^2 N)$.

This is the same formula as the simplified expression above.

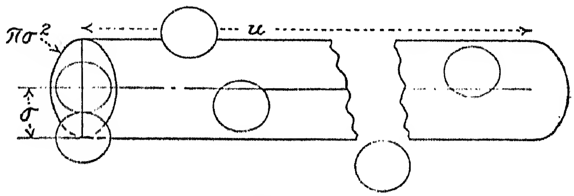

FIG. 5.

17. Relative-velocity Correction.—In Sec. 14, when the mean number of collisions per second experienced by a particular molecule was being evaluated, one assumption was tacitly made, correction for which will now be developed. In computing the probability of collision of a point A with an element of the surface S, the speed of approach of the point A to the element dS was taken simply as the root-mean-square speed of the molecules.

Actually, the quantity which should be used is the mean *relative speed* of the point A and the surface S. Now part of the surface S is that which is parallel to the walls of the vessel. The mean relative speed of the point A with respect to the walls is simply the root-mean-square speed of the molecules as used. The principal part of S, however, consists in the spheres of radius σ which surround all of the other molecules. In the preceding derivation, when these were regarded as at rest, the relative speed of A and of this part of S was correctly taken as u. It is now necessary to examine the effect of making a hypothesis more in accord with

the facts—that the other molecules are also moving in all directions with the same* *mean speed* equal to u.

This requires that the mean relative speed of two molecules which each move with the same speed, but for which all directions of motion are equally probable, be calculated. The relative speed of two molecules is the vector difference of their speeds when these are referred to the same reference system (Fig. 6). If θ is the angle between the directions of motion, the magnitude of this vector difference ξ is evidently given by

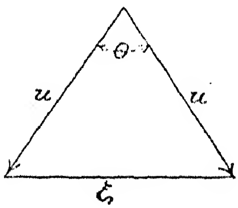

FIG. 6.

$$\xi = 2u \cdot \sin \frac{1}{2}\theta,$$

since ξ is the base of an isosceles triangle, whose two equal sides are each equal to u, and in which the angle opposite ξ is θ. ξ is to be averaged over all values of θ, taking account of the equal weighting of the solid angle in the various directions around the vertex of θ. This is accomplished as before (Sec. 11) by multiplying ξ by $2\pi \cdot \sin\theta \cdot d\theta$. Integrating from 0 to π, and dividing by 4π, the mean value ξ is then

$$\bar{\xi} = \frac{1}{4\pi}\int_0^\pi 2u \sin\frac{1}{2}\theta \cdot 2\pi \sin\theta d\theta = 2u\int_0^\pi \sin^2\frac{\theta}{2}\cos\frac{\theta}{2}d\theta$$
$$= \frac{4u}{3},$$

or the mean speed of the molecules relative to each other is four-thirds their root-mean-square speed when all the molecules are treated as moving with the same speed.

Returning to the equation of Sec. (16) for the mean number of collisions per second, it is seen that this can better be written:

$$n_1 = \frac{u\Sigma}{4(V - b)} + \frac{\frac{4}{3}\pi\nu\sigma^2 u}{V - b},$$

the first term representing collisions with the walls and the second collisions of the molecules with each other introducing the relative-velocity correction. Supposing as before that Σ is negligible in comparison with the area of the spheres of exclusion, a new expression is obtained for the free path as follows:

* This assumption of equal molecular speeds introduces an error which will later need modification (see Sec. 37, Chap. IV).

$$L = \frac{V - b}{\frac{4}{3}\pi\nu\sigma^2}.$$

Again making the lesser approximation in neglecting b, the expression for the mean free path appears in the form

$$L = \frac{V}{\frac{4}{3}\pi\nu\sigma^2} = \frac{1}{\frac{4}{3}\pi N\sigma^2}.$$

Dividing both sides of the equation by σ, this yields

$$\frac{L}{\sigma} = \frac{1}{\frac{4}{3}\pi N\sigma^3},$$

so that the mean free path bears the same ratio to the diameter of the molecules as does the total volume of the vessel to the total volume of the spheres of exclusion, or as does the total volume to eight times the volume of the molecules.

The free-path expressions which have been obtained by correcting for the mean relative speed are the same as given originally by Clausius in 1858. In their derivation it is to be noticed that the molecules are regarded as all having the same speed u, all directions of motion being regarded, however, as equally probable.

18. Clausius' Pressure-volume Relation.—In Chap. II, the deduction of the equation embracing the experimental results of Boyle and Charles was based on the original method of Joule, who found it necessary to regard the molecules as all having the same speeds, and certain fractions of them moving perpendicularly to each of the walls of the containing box. By arguments similar to those used in arriving at the mean free path, Clausius was better able to face the facts by supposing all directions of motion equally probable in giving a theoretical deduction of this equation. He was, however, still bound to the assumption that all the molecules travel with the same speed. The number of collisions per second which each molecule makes with S, in which the molecule strikes at an angle between θ and $\theta + d\theta$ with the normal to S, was found by Sec. 14 to be

$$\frac{Su \sin\theta \cos\theta d\theta}{2U}.$$

If ν molecules are contained in the available volume, $V - b$, the number of collisions is

$$N_{s\theta} = \frac{S\nu u \sin\theta \cos\theta d\theta}{2(V - b)}.$$

From the dynamics of perfectly elastic collisions between smooth bodies, it is known that when a smooth elastic sphere collides with an elastic plane the normal component of the momentum of the ball is reversed while the tangential component is unaffected. In having the normal component of its momentum reversed, the ball communicates to the wall an impulse equal to the total change of momentum which is evidently twice the normal component. If the velocity of the molecule of mass m relative to the wall is u, the normal component of the velocity is $u \cdot \cos\theta$, so that the impulse communicated to the wall at each collision is

$$2mu \cos\theta.$$

The impulse communicated per second, *i.e.*, the force exerted by all the molecules which collide at an angle between θ and $\theta + d\theta$, is

$$f_\theta = \frac{2\nu S u^2 m \cos^2\theta \sin\theta d\theta}{2(V - b)}.$$

As collisions occur only when $\theta < \pi/2$, the force exerted on the surface by all the collisions will be obtained on integrating this expression with respect to θ from 0 to $\pi/2$.

$$\int_0^{\frac{\pi}{2}} f_\theta d\theta = \frac{\nu S u^2 m}{V - b}\int_0^{\frac{\pi}{2}} \cos^2\theta \sin\theta d\theta = \frac{\nu S u^2 m}{V - b}\left[\frac{\cos^3\theta}{3}\right]_0^{\frac{\pi}{2}} = \frac{\frac{1}{3}\nu m u^2 S}{V - b}.$$

The pressure exerted by the gas on the walls is the force per unit area, so that the last expression leads to the following expression for the relation between the pressure and volume of a gas:

$$p(V - b) = \frac{1}{3}\nu m u^2.$$

This is the theoretical equation as developed by Clausius.

Comparing the Clausius equation with that of Joule (Sec. 5), it is seen that the two correspond exactly except that the Clausius equation makes provision for the term b, representing the influence of the finite size of the molecules. Following upon the pioneer work of Boyle, experimenters found that there were small deviations from the inverse proportionality of pressure and volume. These slight deviations have their origin in two things:

(1) the finite size of the molecules, and (2) cohesive forces acting between the molecules in addition to those which come into play during collisions. The Clausius equation shows how the first should affect the pressure-volume relation. The way in which the second acts will, of course, depend on the nature of the supposed intermolecular forces. This point will be given detailed discussion later (Sec. 48, Chap. V).

19. The Quantity b.—This quantity, which occurs in the free-path expressions as well as the pressure-volume equation of the gas, was first introduced in Sec. 15 simply as the difference between the actual volume of the vessel and the somewhat smaller volume which is available for the motion of the point A. It was there seen to be made up of a thin layer along the walls of the vessel and a part which depends in some way upon the volume of the molecules themselves.

It is now desirable to take up the study of the way in which b depends on the volume of the molecules. This amounts to a complete determination of b for all practical purposes, since the contribution of the layer along the walls is negligible. At first sight, it might be supposed that b for the gas in 1cm^3 at N.T.P. is simply equal to the total volume of the spheres of exclusion. Since these are spheres of radius equal to the diameter σ of the molecules, this would give

$$b = \frac{4}{3}\pi N\sigma^3,$$

where N is the number of molecules per cm.^{3}

Actually, however, b is only one-half of the value given. This may be seen to be the case by considering the collisions of a single molecule of radius equal to that of the sphere of exclusion, *i.e.*, equal to the diameter of the molecules, with the points which represent the centers of the other molecules. In a collision of such a sphere with a point only that half of the sphere which is directed toward the line of relative motion of sphere and point is active in excluding the point from a volume. This is exactly true for binary encounters between molecules. It is conceivable that there is occasionally a collision in which three or even more molecules are involved at once, but it may be shown that such cases are extremely rare. The correction due to ternary and higher collisions is quite unimportant in comparison with the approximation already made in assuming spherical molecules.

The value of b is then to be taken as

$$b = \frac{2}{3}\pi N\sigma^3.$$

As will later be seen, b can be experimentally determined, and hence if N is known, σ may be evaluated. The deduction makes it possible, however, to use this relation only down to gas volumes of $\frac{4}{3}\pi N\sigma^3$ or $2b$, since for volumes less than this the equal probability of all kinds of impacts is altered by the limitations of the space available. According to Van der Waals, such a change in the value of b actually occurs for gas volumes less than $2b$, as will be seen in Sec. 52.

20. Number of Molecules Striking Unit Surface per Second. It is often of interest to determine the number of molecules striking a surface per second. The knowledge of this quantity is very useful in calculations of heat transfer to solid surfaces and for problems of evaporation when equilibrium exists. In this section two short deductions will be given. In the next chapter a more rigorous deduction will also be given involving the distribution of the free paths and the velocities among the molecules.

In Sec. 14 it was found that the chance P_s of a single molecule striking a surface S per second was $P_s = Su/4U$, where u is the average velocity and U the volume of the vessel.* If there are n molecules in U the number striking S per second is given by $P_s n = N_s$. Thus $N_s = nSu/4U$, and calling $n/U = N$ the number of molecules per cm³, $N_s = SNu/4$. If $N_s/S = N_1$, the number striking a cm² per second, then

$$N_1 = \frac{Nu}{4}.$$

Again it is possible to proceed as follows. Assume a cm² of surface with N molecules per cm³ in the space above it. Of these molecules the chance that one has a velocity so directed as to make an angle θ with the normal to the surface is $\sin\theta d\theta/2$ (see Sec. 14). Of the N molecules in a cm³ only those which lie in a parallelopiped u cm long and of base $1 \times \cos\theta$ cm² will strike the surface in 1 second, for those further away will not reach it in 1 second going u cm/sec.; and only those that lie in the cylinder whose base has the area normal to the direction of motion $1 \times \cos\theta$ cm² can strike it at an angle θ with the normal. Thus if there are N molecules per cm³, only those in the volume $u\cos\theta$, to wit, Nu

* Note that here the volume U is used interchangeably with V which is permissible as b is very small.

cos θ, will be in a position to strike the surface, and of these the chance of striking the surface at θ is sin $\theta d\theta/2$. Hence the number striking at an angle θ is given by

$$N_\theta = u \cos \theta \frac{N}{2} \sin \theta d\theta.$$

Integrating θ from 0 to $\pi/2$ to cover all space above the surface, the result is

$$N_1 = \frac{Nu}{2} \int_0^{\frac{\pi}{2}} \sin \theta \cos \theta d\theta = \frac{Nu}{4}.$$

21. The Distribution of Free Paths.—The conception of the average, or mean, free path recently deduced gave the *average value* of the distance which a molecule had to move between two successive impacts. It was assumed in the process of averaging that the motion of the molecule in any direction was equally probable, and that the molecule might be at any point in the volume. That is, it was assumed that enough points and directions were taken in averaging in order to permit this to hold true. Actually, in looking at one of the instantaneous pictures of the surfaces of exclusion surrounding the point molecule A (Sec. 14), the molecule is pictured surrounded by a very irregular surface. If, then, from any point A where it happened to be this molecule were to move in a direction AC (Fig. 2) it would strike the wall after having traversed a very short stretch. If, however—what is equally probable—the point molecule should move in the direction AB, the distance moved before impact would be quite long. Thus, while a mean value for the free path is spoken of, the paths actually traveled are not equal, but may take on any value. The fact that these paths depend on pure chance for their single values will make it possible to derive an expression giving the distribution of the paths among the molecules.

The law of distribution of free paths may be derived as follows: Consider I molecules starting out from a collision. After these have gone a distance x the number which have not yet experienced a collision is denoted by y. If a molecule, on the average, has Z collisions per second and its speed is u, the probable number of collisions in 1 cm is Z/u and the probable number of collisions in going a distance dx is $(Z/u)\, dx$. This is, however, equal to the decrease in y, *i.e.*, to $-dy$, for y decreases as x increases. Therefore, it is possible to write $dy = -\frac{Z}{u} y dx$.

Separating the variables, $dy/y = -(Z/u)\,dx$, and integrating between the limits $y = I$ at $x = 0$, and $y = y$ at $x = x$, the result is $\log y - \log I = -Zx/u$,

or
$$y = Ie^{-\frac{Z}{u}x}$$
and
$$dy = -\frac{Z}{u} Ie^{-\frac{Z}{u}x}\,dx.$$

It is important to note in this place that in deducing this equation the tacit assumption was made in writing $dy = -\frac{Z}{u}y\,dx$ that the chance of a collision depended on $\frac{Z}{u}y$ and dx only. That is, the number of impacts dy was governed by the distance traversed dx, by the number of molecules traversing it, and by a constant factor which gives the probable number of molecules experiencing a collision in 1 cm. This constant is what might be called a "scale factor" and is the constant of proportionality which determines the absolute value of the path. The derivation therefore assumes the independence of the free path executed from all other factors than y, dx, and Z/u.

To obtain a meaning for the constant Z/u it merely becomes necessary to determine the average free path, or mean free path L. This is obtained by multiplying the number of molecules dy of path between x and $x + dx$ by x, the length of the path, summing it for all the groups of molecules from 0 to I, and dividing by I. Thus the mean free path,

$$L = \int_0^I \frac{x\,dy}{I} = \int_\infty^0 -\frac{I\frac{Z}{u}e^{-\frac{Z}{u}x}}{I}\,x\,dx.$$

$$L = -\frac{Z}{u}\left[-\frac{xe^{-\frac{Z}{u}x}}{Z/u}\right]_\infty^0 + \frac{Z}{u}\int_\infty^0 \frac{-e^{-\frac{Z}{u}x}}{\frac{Z}{u}}\,dx = \frac{u}{Z}.$$

Hence $L = u/Z$ and the equations above become

$$y = Ie^{-\frac{x}{L}}.$$
$$dy = -\frac{I}{L}e^{-\frac{x}{L}}\,dx.$$

Thus out of I paths that start anew after their last collision $Ie^{-\frac{x}{L}}$ have a path exceeding x cm in length. The larger the value of L, the average path, the more paths there will be that exceed a given

x. The number dy out of the I paths that end in a specific fractional interval dx/L of the mean free path (*i.e.*, in a certain interval between x and $x + dx$ whose length is a fraction dx/L of the mean path L) is $Ie^{-\frac{x}{L}}\,dx/L$. Thus by choosing an adequate interval dx/L the number of impacts suffered in that interval can be found. It may be seen from the equation that both the curves for y and dy as a function of x are exponential curves. At the point $x/L = 0$, $y = I$, and at increasingly large values of

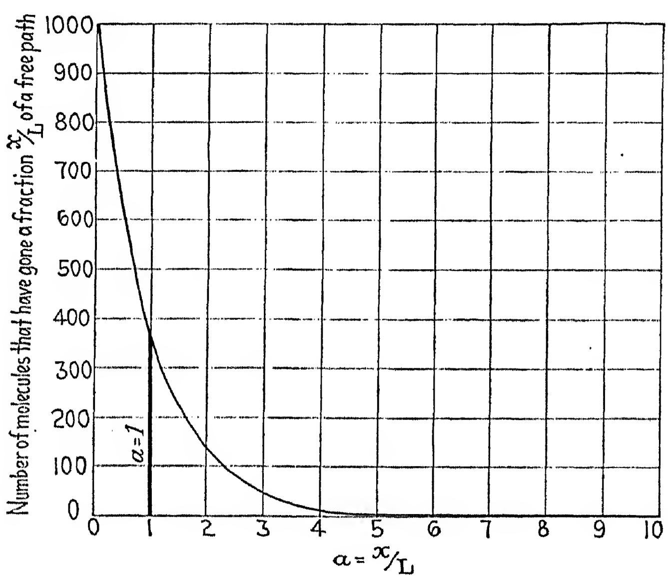

FIG. 7.

x/L, y approaches 0 asymptotically. The curve for y as a function of x/L is given in Fig. 7. Thus it can be seen from Fig. 7 that out of 1000 molecules starting at $x = 0$, 670 go a distance $x/L = 0.40$, 370 go a distance $x/L = 1$, and 18 go a distance $x/L = 4.02$. The point marked in the Fig. 7 by the vertical line is the point at which $x/L = 1$. It is the point where x equals the mean free path and it is the center of gravity of the distribution curve. It is to be noted that in this distribution curve the free paths have all values and are not grouped closely on either side of the mean value as will be found to be the case for the distribution of velocities (Sec. 35, Chap. IV).

22. The Mobility of Gaseous Ions (an illustrative application of the free-path distribution). — As an example of the use of the concept of the free paths and of the importance of taking into account the distribution of the free paths, the evaluation of the velocity of gaseous ions deduced on the kinetic theory may be used. The normal gas ion, the carrier of electricity in gases, could be assumed to consist of a single molecule* carrying an extra positive or negative charge (see Sec. 104 of Chap. XI).

If such a charged molecule be placed in a field of strength X volts per cm in a gas it would experience the acceleration Xe/m due to the action of the field, where e is its charge and m its mass. The acceleration cannot last for a long time, however, as the ion soon collides with a neutral molecule of its own mass. If a large number of such impacts be regarded, it may be assumed (see Sec. 105) that at each impact the velocity gained by the ion in the direction of the field is annihilated. It must then begin its acceleration in the field anew after each impact. If the ion makes many millions of collisions in going a centimeter in the direction of the field this will result in the ions having a uniform average velocity of drift in the direction of the field. This velocity reduced to unit field strength is called the "mobility" of the ion. This reduction assumes velocity proportional to field strength, a fact borne out by experiment. It is thus obvious that the mobility must largely depend on the acceleration over a mean free path, and that hence the mean free path must be an important feature in the evaluation of the mobility. In deducing the expression for mobilities as here given the following assumptions must be made:

1. Ions do not exert forces on the neutral molecules, *i.e.*, the paths are not influenced by the ionic charge.
2. The impacts between ions and molecules as between molecules and molecules are perfectly elastic.
3. The mass of the molecule equals that of the ion.
4. The field is so weak that the gain in energy of the ion from the field over a single free path is small compared to the energy of agitation of the gas molecules.

* The nature of the ion is not as yet certain; and it is a question whether it is a single charged molecule or *a group of molecules about a charged* molecule. For simplicity it is assumed here that it is merely a charged molecule of the gas.

Let an ion go an average path L in a time T, where T can be evaluated from $T = L/u$, u being the average velocity of thermal agitation of the molecules.

The distance S_t traversed by the ion in the direction of the field in virtue of its charge in a time T is given by

$$S_t = \frac{1}{2}aT^2 = \frac{1}{2}\frac{X\epsilon}{m}\frac{L^2}{u^2},$$

for $a = \frac{X\epsilon}{m}$, where ϵ is the charge, X the field strength and m the mass.

Now if the ion goes S_t in the direction of the field in T seconds its average velocity of drift in the field will be

$$\bar{v} = \frac{S_t}{T} = \frac{1}{2}\frac{X\epsilon}{m}\frac{L}{u}$$

or its mobility will be $K = \frac{\bar{v}}{X} = \frac{1}{2}\frac{\epsilon}{m}\frac{L}{u}.$

Now in this deduction the value of an average free path L was assumed and all paths were assumed to be equal. Actually, the paths are not all equal and in this case the assumption introduces a serious error, for the distance traversed during the time t is proportional to t^2. Thus, for a long path L, $t^2 = (x/u)^2$ would give a very different S_t than for a short path. The distribution of free paths must then be considered. Replacing T by t and L by x in the expression for S_t above,

$$S_t = \frac{1}{2}\frac{X\epsilon}{m}\frac{x^2}{u^2},$$

where x refers to all paths ending between x and $x + dx$. Now out of I initial paths the number of the length x is given by $-dy$ or $\frac{I}{L}e^{-\frac{x}{L}}dx$. Hence the average S_t is given by

$$\bar{S}_t = \frac{1}{2}\frac{X\epsilon}{m}\frac{\int_0^\infty \frac{x^2}{u^2}\frac{I}{L}e^{-\frac{x}{L}}dx}{I},$$

Whence $\bar{S}_t = \frac{1}{2}\frac{X\epsilon}{m}\frac{1}{Lu^2}\left[-Lx^2e^{-\frac{x}{L}} + 2L\int xe^{-\frac{x}{L}}dx\right]_0^\infty$

$$\bar{S}_t = \frac{X\epsilon}{2Lmu^2}[2L^3] = \frac{X\epsilon L^2}{mu^2}.$$

As the number of paths of an ion in going 1 cm is very great, the average time of a path may safely be taken as $t = T = L/u$; hence the expression for the velocity becomes

$$\bar{v} = \frac{S_t}{T} = \frac{XeL}{mu}$$

and the mobility is

$$K = \frac{eL}{mu},$$

in contrast to the value $K = \frac{1}{2}\frac{e}{m}\frac{L}{u}$ obtained in neglecting the distribution of free paths.

23. Experimental Knowledge of Molecular Free Paths. The manner in which the free-path concept has been verified must for part of its details be postponed to Chap. VI, in which relations are deduced which involve the free path in such a form that it can be evaluated from experimental measurements. The relations involve the kinetic-theory deductions for the physical constants known as the coefficients of viscosity, of diffusion, and of heat conductivity of the gas. All these equations, although they have some uncertainty in the value of the numerical coefficients concerned in them, give nearly the same values for L. Again, the theory says that L should be related to σ, the diameter of the gas molecules, and to N, the number of molecules in a cm³. In recent years σ[1] has been determined in a variety of ways and N[2] has been accurately determined. The values so obtained, in so far as they theoretically should agree, agree well with the values of L determined directly from viscosity.

The two best experimental proofs, however, depend on more direct measurements of the free paths and distribution of free paths. The first method is due to M. Born.[3] It depends on the measurement of the thickness of a silver film deposited on a glass plate out of a beam of silver atoms moving in an atmosphere of air at reduced pressures as a function of the distance x from the origin of the beam. The apparatus is schematically sketched in Fig. 8. From the small heated tip of the quartz tube A a stream of evaporating silver is reduced to a narrow beam by means of the tube B. From there the stream passed through a circular hole in each of four brass discs one above the other and 1 cm apart. These discs were cooled by liquid air about the upper portion of the quartz tube. Each of them supported a

glass quadrant P_1, P_2, P_3, or P_4 whose apex extended to the center of the circular opening. Each quadrant in turn was rotated through 90 deg. relative to the preceding one. Thus each of four cold glass screens at distances of 1 cm apart received one-fourth of the beam on their tips. The quartz tube was connected to an adequate pumping system and a set of gages for measuring and controlling the gas pressures was provided. The experiment then consisted in evaporating the silver at various pressures and measuring the relative amount of silver deposited on each plate as a function of the distance between the plates. The measurement was accomplished by a photometric comparison of the density of the deposits on the separate plates.

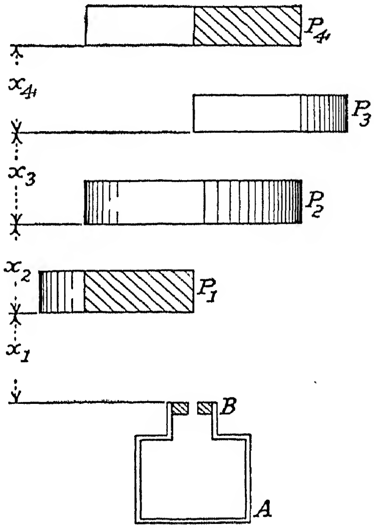

Fig. 8.

The test of the theory by the experiments follows. If the equation for the distribution of free paths is correct, then the density of deposit should be given by

$$D = D_0 e^{-\frac{x}{L}},$$

where x is the distance between the plate and the origin B of the ray and L is the mean free path. In practice, however, even at the lowest pressures obtainable, there is a slight change in density on the different plates due to a geometrical spreading of the beam. Thus to eliminate this difficulty the measurements were made as follows: The values of the density D_{10} when there was no gas present and the free path had the length of the chamber, and the density D_1 on the same plate when the gas was present giving a free path L, are given by

$$D_1 = D_{10} e^{-\frac{x_1}{L}}$$

for one plate. For another one of the plates it is given by

$$D_2 = D_{20} e^{-\frac{x_2}{L}}$$

where x_1 and x_2 are the distances of the plates from the source (*i.e.*, the point B).

Therefore

$$L = \frac{x_2 - x_1}{\log\left(\frac{D_1 D_{20}}{D_2 D_{10}}\right)}.$$

In the actual experiments reported, $x_2 - x_1 = 1$ cm. These gave in one series of measurements the following values:

for $p = 5.8 \times 10^{-3}$ mm, $L = 1.7$ cm.
$p = 4.5 \times 10^{-3}$ mm, $L = 2.4$ cm.

This gives pL constant within the limits of experimental error and so verifies the prediction of the kinetic theory. The values obtained for L if reduced to atmospheric pressure are then $L = 1.3 \times 10^{-5}$ and $L = 1.4 \times 10^{-5}$ cm. From viscosity measurements on L for air, the gas used here, $L = 0.99 \times 10^{-5}$ cm, while for Hg, which is a monatomic gas like Ag vapor, $L = 2 \times 10^{-5}$. Thus for the Ag atoms in air the value obtained by direct measurement is in excellent agreement with the other values, considering the difficulty of the experiment.

In a recent repetition of Born's experiment performed with great care, F. Bielz[4] has determined σ for collisions between silver atoms and N_2 molecules. The particular improvements in this work lay in the method of introducing the glass plates for catching the silver atoms, in the corrections for the spreading of the beam, and in the developing and measuring of the thickness of the deposit. In testing the law of distribution of paths, the free path L was calculated by means of the equation $D_x = D_0 e^{-\frac{x}{L}}$ from the measurements on the thickness of the deposit D_x at different values of x. The values of L multiplied by the pressures for different values of D should be constant. Three different values of x were used—22, 32, and 42 mm—and the following values for pL were obtained, 0.0132, 0.0104, 0.0097, 0.0109, 0.0094, 0.00945, with a mean of 0.0098. This degree of constancy, when considered in the light of the other experimental uncertainties, establishes the distribution law quite successfully. The value obtained for σ, the molecular diameter, is 2.58×10^{-8} cm, with an accuracy of 5 per cent. If $r = \frac{1}{2}\sigma$ for N_2 be taken as 1.55×10^{-8} cm, σ for the Ag atom is 1.0×10^{-8} cm.

24. Electron Free Paths.—In the preceding work the mean free path for gas molecules was deduced assuming molecules of diameter σ moving among like molecules. The value for L was

given by the expression $L = \frac{1}{\left(\frac{4}{3}\pi\sigma^2 N\right)}$, where σ is the diameter of the molecules, and the factor $\frac{4}{3}$ came in from a consideration of the relative velocities of the molecules. As will be seen later (Sec. 37, Chap. IV), if the distribution of the velocities be considered, the mean free path is given by the expression

$$L = \frac{1}{\sqrt{2}\pi\sigma^2 N},$$

where the $\sqrt{2}$ replaces the $\frac{4}{3}$ above. Now for an electron whose dimensions (3×10^{-13} cm) are minute compared to σ (2×10^{-8} cm) and whose velocity of agitation is much greater than that of the molecules (see problem 1, Chap. II), the equation may be simplified. For a point electron the sphere of exclusion has a radius $\sigma/2$ (*i.e.*, the radius of the molecules), for it can move right up to the surface of the assumed spherical molecules. Also the electron moves so much more rapidly than the molecules, since it has the same energy of agitation (as demanded by the law of equipartition) while it has less than $\frac{1}{3600}$ the mass of most molecules, that the latter can be considered at rest relative to it. Hence the correction for relative velocities may also be removed. The equation for the electron free paths L therefore becomes

$$L_1 = \frac{1}{\pi(\sigma/2)^2 N}$$

and

$$L_1 = 4\sqrt{2}L$$

for the molecules.

25. Distribution of the Electron Free Paths.—It is possible to obtain a beam of electrons of almost any velocity and to shoot them through a gas. At any point of the gas the number of electrons can be measured and compared with the number at any other point by measuring, with an electrometer, the charges delivered by the electron beam per unit time in a Faraday cage. Now it also happens that electrons that are thrown out of the beam by colliding with molecules and being deflected by the impact, or those which have collided and lost appreciable velocities in the process, can be excluded from the measuring chamber. Thus it should be possible to measure y, the number of electrons which have escaped collision at any point of the path

x cm from the source, as a function of x. This would at once furnish an exceptional means of testing the distribution law.

The first man to test this was Lenard,[5] who even before his critical paper in 1903 had found that the number y of electrons at a distance x from the source moving in a beam in a gas at a pressure p could be accurately represented by an equation of the form

$$y = Ie^{-\alpha x}.$$

In this case α is a constant related to the free path L in a manner to be discussed later. This law he verified for a large range of pressures p and distances x. It holds well for electrons of velocities ranging from near that of light down to velocities of the order produced in electrons which have fallen through a potential difference of less than a volt. With varying velocities, however,

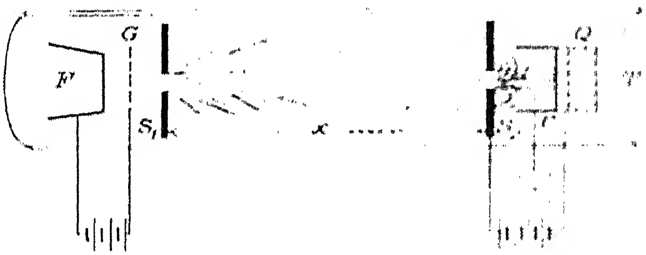

FIG. 9.

α, and hence the value of L, varies. The significance of this will be seen later.

More recently two men, H. F. Mayer[6] and C. Ramsauer[7] (later Brode[8] and Rusch[11]), have carried on very refined measurements of this quantity at low velocities where the mean free paths of electrons should approach kinetic-theory values. The diagram of Mayer's experimental arrangement may be seen in Fig. 9. From the glowing filament F electrons arise and are given a velocity v by means of the field between the gauze G and F. They then shoot in a nearly parallel beam through the small hole in the screen S_1. From there they traverse the gas space to a screen S_2 which is close to the Faraday cylinder C which is connected to the electrometer. The whole is placed in a glass tube T in which the gas pressure can be varied at will and accurately recorded. The distance x from C and S_2 to S_1 can be varied by moving C and S_2 back and forth by an electromagnet outside of the tube, C being attached to a small piece of soft iron Q. Between C and S_2 is

placed a retarding potential difference of about 0.95, of the initial potential driving the electrons from F to G. Thus if an electron having energy equivalent to the potential difference from F to G loses more than 5 per cent of its energy by impact with a molecule it will never be able to reach C against the field S_2C. For this apparatus the equation for y as a function of x, can be written as

$$y = f(x)I_0e^{-(a+\alpha p)x}$$

assuming that the experimental law of Lenard is correct. Here $f(x)$ is a small variation of the number of electrons with the distance x due to a spreading of the electron beam as a result of the mutual repulsion of the electrons. It is, on the whole, a function of the velocity of the electrons. The constant a is the constant for the absorption or scattering of the electrons by the residual gas in the apparatus when the pressure is at its lowest; α is the specific absorption of the gas and depends on the diameters of the molecules or, better, is a function of L; p is the gas pressure. Mayer in his experiment changed p and x and eliminated the factors $f(x)$, a, and I by four measurements. This was essential, as I changed some with the gas pressure due to cooling of the filament.

At a pressure p_1 the currents I_{11} and I_{12} were measured at distances x_1 and x_2, and at p_2 the currents I_{21} and I_{22} were measured for distances x_1 and x_2. Then

$$I_{11} = f(x_1)I_{10}e^{-(a+\alpha p_1)x_1}.$$
$$I_{12} = f(x_2)I_{10}e^{-(a+\alpha p_1)x_2}.$$
$$I_{21} = f(x_1)I_{20}e^{-(a+\alpha p_2)x_1}.$$
$$I_{22} = f(x_2)I_{20}e^{-(a+\alpha p_2)x_2}.$$

$$\text{Call } \Delta_1 = \log \frac{I_{11}}{I_{12}}, \text{ and } \Delta_2 = \log \frac{I_{21}}{I_{22}},$$

whence

$$\alpha = \frac{\Delta_2 - \Delta_1}{(p_2 - p_1)(x_2 - x_1)}.$$

This gives the constant α per mm pressure if p_2 and p_1 are in millimeters, and per cm path difference if x_2 and x_1 are in centimeters. For a pressure p mm, "a" $= \alpha p$, where "a" is the constant of an equation giving the number of electrons which escape molecular encounters in going x cm in the gas. In its simple form, disregarding the correction terms for experimental difficulties above, the equation is

$$y = Ie^{-\text{``}a\text{''}\,x}$$

and comparing it with the free-path equation derived for molecules,

$$y = Ie^{-\frac{x}{L_1}},$$

it is seen that $\alpha p =$ "a" $= 1/L_1$,

as
$$L_1 = \frac{1}{\pi\left(\frac{\sigma}{2}\right)^2 N} = \frac{1}{\text{"}a\text{"}}$$
$$\text{"}a\text{"} = \pi\left(\frac{\sigma}{2}\right)^2 N,$$

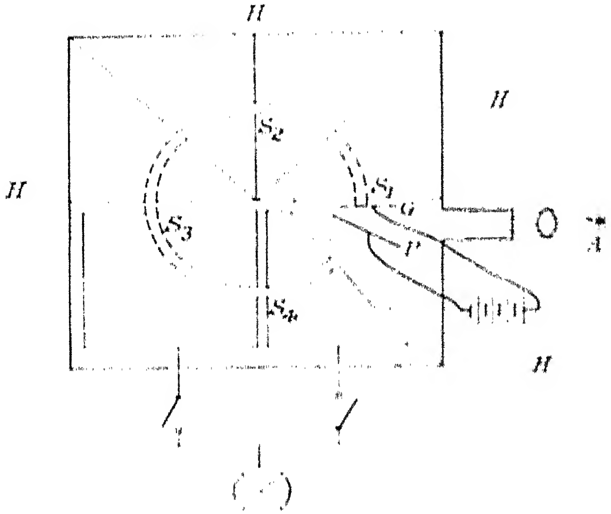

FIG. 10.

i.e., it is the total absorbing area, or area of cross-section, of the molecules in the volume in which there are N molecules. Thus the fact that "a", and hence L_1, are constants for any gas independent of x and p establishes once and for all this relation and proves the legitimacy of the assumption of the distribution of free paths.

A method even more sensitive than this one is due to Ramsauer. In this case photoelectrons liberated from a plate P by light from an arc A are given a velocity by a field between a gauze G and the plate P. After passing through a slit S they are bent into a circular path by a uniform magnetic field H perpendicular to the plane of Fig. 10. By means of a series of narrow slits S_2, S_3, and

S_4, the electrons of one velocity are kept in the beam by the field; all others (*i.e.*, those having different curvatures) are screened out. Two insulated chambers corresponding to the third and fourth quadrants and bounded by the slits ~~and~~ S_3 and S_4 are connected so that they can have their charges read on two electrometers. Call x_3 and x_4 the distances from the screen S_1 to the screens S_3 and S_4. Call I_1 the current received by the fourth quadrant and i_1 the sum of the currents received by the third and fourth quadrants together at a pressure p_1. Call I_2 and i_2 the corresponding currents for a pressure p_2. Then from similar reasoning to that of Mayer

$$\alpha = \frac{1}{(p_2 - p_1)}\frac{1}{(x_4 - x_3)} \log\left(\frac{\frac{I_1}{i_1}}{\frac{I_2}{i_2}}\right).$$

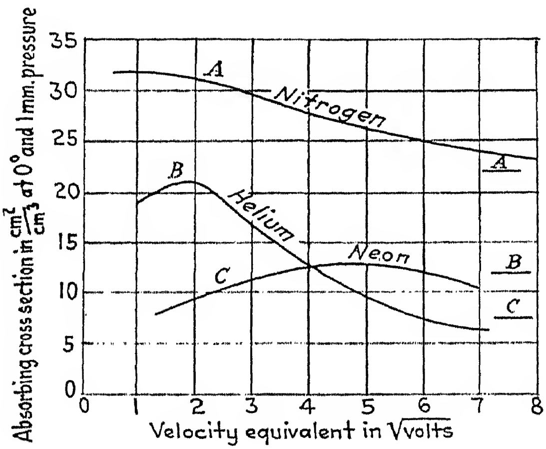

Fig. 11.

The chief difference between the two measurements is that, owing to the critical elimination due to the path of the rays in the field, only those electrons get through which have suffered practically no loss of energy or change in direction. The results agree for both methods well within the limits of error, when the velocities are low (*e.g.*, about 10 to 15 volts). By volt velocity is meant the equivalent potential through which an electron must fall freely to gain the velocity.

The curves obtained by Ramsauer for a number of gases are reproduced in Figs. 11 and 12, the quantities plotted are "a" per

mm pressure per cm³ against the square root of the equivalent potential applied to give the electrons their speed. The values for "a" computed directly from "a" $= \frac{1}{4\sqrt{2}L}$, where L is obtained from viscosity measurements, are indicated by the straight lines on the right of the figure.

It is seen that in order of magnitude the values of "a" at the higher speeds are nearly the same as those for "a" computed from kinetic theory. For still higher speeds, "a" decreases rapidly as the velocity increases. This is easily explained, since it is only for lower speeds that the collisions of electrons with molecules are elastic and they are deflected by the surfaces of the molecules. At higher speeds the electrons begin to shoot through

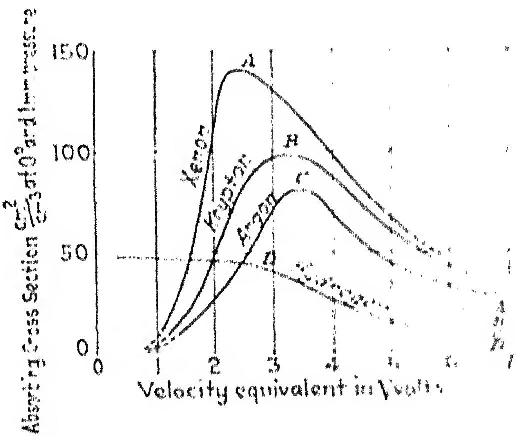

FIG. 12.

the molecules. The behavior at the lower velocities is nearly normal for all but the inert gases. At speeds near those exciting characteristic resonance effects in the electrons of the atoms or molecules themselves, the bombarding electrons, especially in the inert gases, seem to be much more readily deflected than otherwise. Thus the effective areas of the molecules are increased and the mean free paths fall to lower values. At still lower speeds the atoms of argon, neon, krypton, and xenon appear to become more transparent to electrons than the kinetic theory demands. In fact, the area for argon drops to one-fifteenth its kinetic-theory value at the lowest velocities, or the mean free path is multiplied by about 15. The meaning of this is obscure, and is characteristic of the peculiar symmetry of the inert gas atoms.

The other gases appear to show nearly normal free paths as the velocity decreases.

On the whole, then, the electron free paths lead to a brilliant confirmation of the distribution law and agree surprisingly well in magnitude with those computed from molecular free paths and the kinetic theory.

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CHAPTER IV

THE DISTRIBUTION OF MOLECULAR VELOCITIES

26. Introduction. Up to the present is has been assumed that all molecules moved with the same velocity. This assumption is, however, unjustified and it is incompatible with the assumed elasticity of the impacts of the gas molecules, as a little reflection will show. For simplicity, assume that all the molecules have equal masses and a common initial velocity c.* If the necessary assumption be made that the impacts are elastic (an assumption essential to the elementary kinetic concepts as otherwise the heat energy would go into the deformation of the molecules and would not remain as energy of translation), then out of the manifold types of collisions taking place the occurrence of an impact of the type pictured in Fig. 13 can be conceived. A molecule m_1, is moving with a velocity c_1. It is struck centrally by another molecule m_2 of the *same mass* moving at right angles to c_1 with an *equal* velocity c_2. After the impact, m_2 will have given all its velocity c_2 to m_1, which had no component parallel to c_2, for molecules in such an impact merely exchange velocities, as shown in Sec. 28. As a result, m_1 will now possess a velocity c_3 equal in magnitude of $\sqrt{2}c_1$ along the line indicated. m_2 will then have no velocity, while m_1 will have a velocity $\sqrt{2}c_1$. In this impact the *total energy* will be the same as before, for the

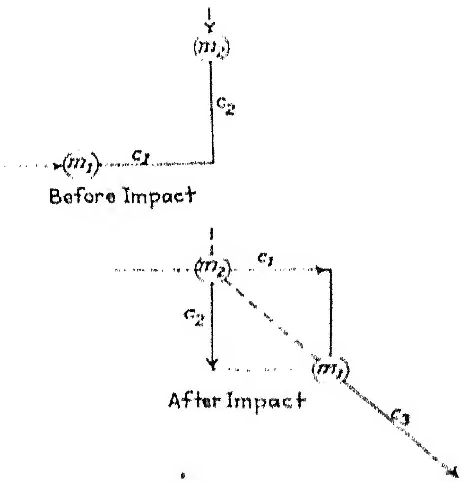

FIG. 13.

* Heretofore the velocity has been designated by the letter u. Since the recognition of the distribution of velocities, molecular velocities will be designated by the conventional symbol c.

initial energy was $\frac{1}{2}m_1c_1^2 + \frac{1}{2}m_2c_2^2 = m_1c_1^2$, since m_1 and c_1 have the same magnitudes as m_2 and c_2, and the final energy will be $\frac{1}{2}m_2(0)^2 + \frac{1}{2}m_1(\sqrt{2}c_1)^2 = m_1c_1^2$. Thus after the first impact in an extreme case, while the energy is conserved, the velocities of the two molecules will no longer be the same. For other impacts the changes will be less, but it is evident that even after a very few impacts the molecules will no longer have the same velocities, and, if enough molecules are taken, molecules with all sorts of velocities will exist. The average velocity $\sqrt{\bar{c}_1^2}$ will, however, remain the same, for $\frac{1}{2}m_1\bar{c}_1^2$ has been conserved, and as long as m_1 is constant c_1 must be constant. Thus the velocities will be distributed about an average value $\sqrt{\bar{c}_1^2}$ which depends, as will be seen, on the temperature of the gas only.

It will be the task of this chapter to deduce this law of distribution of velocities and to give what experimental evidence exists of its verification. The deductions given will be of two sorts.* The first one will be the general approach given by Boltzmann and based on a study of the equilibrium resulting in elastic impacts. The second one will be the original deduction due to Maxwell. In the latter case certain fundamental assumptions made about molecular motions and velocities are such that they fall into a category of *general conditions* in the theory of probabilities such that they lead to the deduction of the distribution law, which must therefore be the distribution law applicable to molecules.

27. Boltzmann's Method.†—The fundamental idea underlying this treatment is that a distribution arrived at by other considerations by Maxwell (Sec. 33), represents the equilibrium state after complete random motion has set in and the velocities have reached their permanent régime of velocities. If this is so, then the distribution law should follow from the condition that in elastic impact the number of molecules having velocities lying between certain limits is constant.

* Still another very ingenious elementary derivation is given in K. F. Hertzfelds, Kinetische Theorie der Wärme, Müller-Pouillets, Lehrbuch der Physik Vol. III, Part II, Chapter Iα, Sect. 7.

† The treatment given here is not a translation of Boltzmann's original deduction.[18] It is a free translation of the very admirable and condensed version of it given by Clemens-Schaefer in his splendid book, "Einführung in die Theoretische Physik."[19]

Let it be assumed that the molecules are rigid elastic spheres and consider those molecules having velocity components between u and $u + du$, v and $v + dv$, and w and $w + dw$, where u, v, and w represent the velocities along the x-, y-, and z-axes. Geometrically considered, these may be represented as those molecules for which the velocity vectors drawn from a point O in Fig. 14 all end in the small volume element $dudvdw$. Assuming that a distribution law exists and that there are n molecules all told, the number ending in $dudvdw$ can be written as $nf(u, v, w)$ $dudvdw$. Here $f(u, v, w)$ represents the function expressing the Maxwellian distribution which it is desired to find. For the sake of brevity let these particular molecules be known as molecules of type A. Per unit volume there are $Nf(u, v, w)\,dudvdw$ of these, where N is the total number of molecules per cm^3. As molecules of type B such molecules may be considered as have velocities lying in a volume element $du'dv'dw'$, *i.e.*, with velocities between u' and $u' + du'$, v' and $v' + dv'$, and w' and $w' + dw'$. The number of molecules of the type B per unit volume is, similarly,

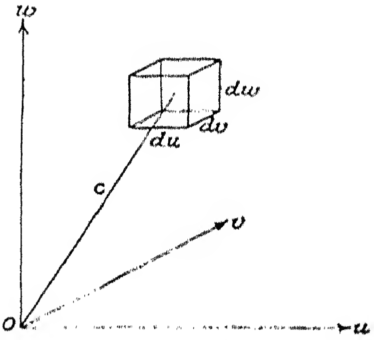

Fig. 14.

$$Nf(u', v', w')du'dv'dw'.$$

The molecules which were at a given instant of type A before an impact change their velocities in a time interval dt as a result of the impacts, while in the same time interval more molecules of other classes as result of impacts enter the type A. *Between these two changes at equilibrium in the gas, an equilibrium must exist, and it is this equilibrium which will define the distribution law.*

One may begin by considering those impacts in virtue of which the *A-type molecules are decreased in number.* Of these impacts it is perhaps simpler not to consider those with all types of molecules and A molecules, but only those between the type-A molecules and the type-B molecules. Impacts between the A- and B-type molecules may now be discussed with an added restriction, namely, that at the instant of impact the lines of centers of the molecules (taken from A to B) have a definite orientation in space. As, however, the A and B molecules have vectors which

end in a finite though small volume $(dudvdw)$. the directions of the lines of centers will vary within certain small limits also, that is, the direction cosines of the line of centers is restricted so as to have components which lie between l and $l + dl$, m and $m + dm$, and n and $n + dn$. If these lines of center were to be depicted as drawn from a common origin, they would for the collisions considered cut out a small surface element dK in a unit sphere drawn about the origin (see Fig. 15). Such collisions will be termed the collisions of type α. To simplify still further the letter F may be written for the product N times the function f. Thus the number of molecules of types A and B per unit volume is given by $F(uvw)dudvdw$ and $F(u'v'w')du'dv'dw'$. And the number of impacts of A molecules with B molecules of the class α in the time dt is given by $\nu_\alpha dt = F(uvw)\ F(u'v'w')\delta^2 c_r \cos \theta dK dudvdw\ du'dv'dw'dt$. This results from a consideration of the nature of the impacts of the molecules considered as spheres. If the molecules have the diameter δ, an impact occurs every

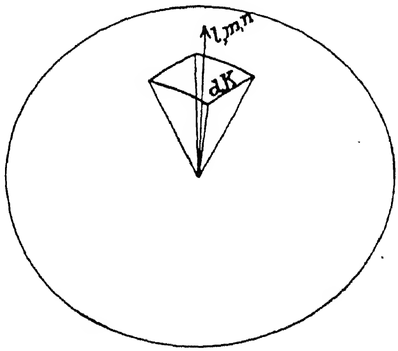

FIG. 15.

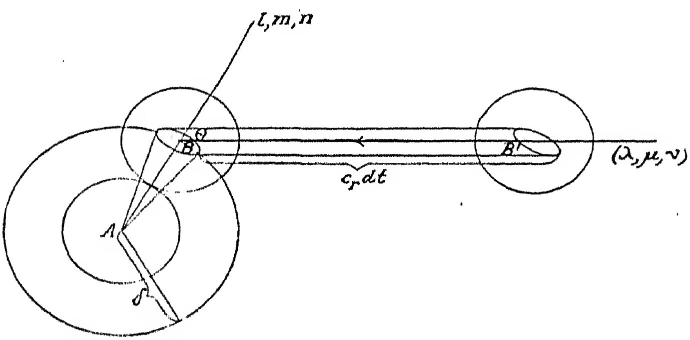

FIG. 16.

time that the length of the line of centers takes on the value δ. In Fig. 16, call A the center of the A molecule and describe a circle of radius equal to the molecular diameter δ about it. An impact then occurs when the center of the B molecule lies on this circle.

In particular, this will be an impact of the α type if the direction $\overrightarrow{AB}$ has the direction cosines l, m, n.

Since dK is the surface cut out of unit sphere by the impacts (*i.e.*, the solid angle), these same impacts will cut out of the sphere of radius δ a surface element δ^2dK. The cone filled by the lines of centers in all the α impacts is shown in the figure. The question now is, How many of the B molecules will collide with A molecules in the time dt? This does not depend on the absolute velocities of the A and B molecules but on their relative velocities. The A molecules may then be considered fixed and the B molecules moving towards them with a velocity c_r. This direction of relative velocity is, obviously, the direction of the straight line $\overrightarrow{B'B}$ and has the direction cosines $\frac{u'-u}{c_r}, \frac{v'-v}{c_r}, \frac{w'-w}{c_r}$, which will be called λ, μ, ν for simplicity. If now there is constructed about $B'B$ as axis an oblique cylinder whose base is the surface element δ^2dK and whose length is $B'B$, then in the time dt only those B molecules which lie in the cylinder will collide with the A molecules. Since $B'B$ is equal to c_rdt, the volume of this cylinder will be $\delta^2dKc_r \cos\theta$, where from the figure $\cos\theta$ is equal to $-(\lambda l + m\mu + n\nu)$. The negative sign comes from the fact that $l\lambda + m\mu + n\nu$ is equal to the cosine of the supplementary angle of θ, and the cosine of the obtuse supplementary angle is negative. Since the volume must be positive, the negative sign must be included in the term for the volume. As per unit volume there are $F(u'v'w')du'dv'dw'$ molecules of the type B, the cylinder contains

$$F(u'v'w')\ \delta^2c_r \cos\theta dKdu'dv'dw'dt$$

molecules. These and only these molecules undergo the α-type collisions with the A molecules in the time dt.

Now there are in a unit volume $F(u\,v\,w)\,dudvdw$ of the A type of molecules present, so that in the time dt the number of impacts of the α type occurring, ν_adt, will be given by

$$\nu_adt = F(uvw)\ F(u'v'w')\delta^2c_r \cos\theta dKdudvdwdu'dv'dw'dt.$$

If, for simplicity, $F(uvw)$ and $F(u'v'w')$ be written merely F and F', then the decrease in the number of A molecules per cm^3 in a time dt through α collisions is given by

$$FF'\delta^2c_r \cos\theta dKdudvdwdu'dv'dw'dt.$$

It is next necessary to determine the increase in the number of A molecules per unit volume in the time dt. To this end another

special type of impacts, which may be termed β impacts, must be regarded. These impacts are defined by the following three conditions:

1. After the impact *one* of the two molecules must belong to type A, that is, its velocity as a result of the impact must lie in the volume element $dudvdw$ of the velocity space.

2. After the impact the second molecule must belong to the type B, that is, its velocity as a result of the impact must lie in the volume element $du'dv'dw'$.

3. At the instant of impact the line of centers should have the direction cosines l, m, n, that is, it must go through the element dK of the unit sphere (Fig. 15). In this case the velocities *after impact* are defined. *It is now necessary to calculate on the basis of the laws of elastic impact the velocities u, v, w and u', v', w' of these molecules before they collided.* This is accomplished by an analysis of elastic impacts which follows.

28. Velocity Exchanges in Elastic Impacts.—Between two rigid molecules of equal masses two types of impacts may occur. The simpler of the two could be termed "head-on collisions," that is, collisions in which the direction of motion coincides with the line of centers at impact. The second type of impact may be termed "oblique impacts," and are such that the direction of motion and the line of centers at impact do not coincide. From the simple laws of impact for the first case the impacts in the second case may be deduced to the extent to which they concern the type of collisions for which they will be used.

Consider two molecules A and B which possess before impact the velocities c and c' along the same line. Let their velocities after impact be $\bar{c}$ and $\bar{c}'$. From the conservation of energy, since the masses are equal, it is possible to write

$$c^2 + c'^2 = \bar{c}^2 + \bar{c}'^2,$$

and from the law of conservation of momentum,

$$c + c' = \bar{c} + \bar{c}'$$

If these equations are written in the following form:

$$c^2 - \bar{c}^2 = \bar{c}'^2 - c'^2$$

$$c - \bar{c} = \bar{c}' - c'$$

division of the first by the second equation yields

$$c + \bar{c} = c' + \bar{c}'.$$

Combining this equation with $c - \bar{c} = \bar{c}' - c'$, the result is

$$\bar{c} = c'$$

$$\bar{c}' = c$$

that is, the two molecules have merely exchanged velocities. Consider next the more complicated case in which the velocities C and C', which now must be considered as vectors, have directions differing from each other as well as from the line of centers AB of Fig. 17. C and C' may be decomposed into two components each, one parallel to the line of centers and the other perpendicular to it. Expressed in another way, C and C' may be decomposed into two vectors C_t and C'_t parallel to the common tangential plane at the instant of impact, and C_n and C'_n normal to this plane. For smooth spheres the tangential components

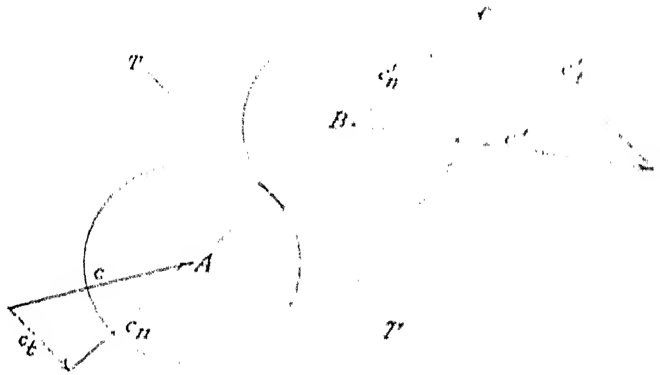

FIG. 17.

C_t and C'_t remain unchanged after the impact, while the normal components play the same rôle as in head-on impacts. If the velocity components after collision be designated, as C_t, C'_t and C_n C'_n, corresponding to the components C_t, C'_t and C_n and C'_n before impact, these facts may be expressed by writing

$$\left.\begin{aligned} C_t &= C_t \\ C'_t &= C'_t \end{aligned}\right\} \tag{1}$$

and

$$\left.\begin{aligned} C_n &= C'_n \\ C'_n &= C_n \end{aligned}\right\}. \tag{2}$$

Since vectorially expressed

$$C = C_t + C_n,$$

Eq. (1) and (2) above lead to the following relations:

$$\begin{aligned} C &= C_t + C_n = C_t + C'_n \\ C' &= C'_t + C'_n = C'_t + C_n \end{aligned} \tag{3}$$

These may be expressed somewhat differently if the relative vector C_r after impact be used, where

$$C_r = C' - C. \tag{4}$$

Since vectorially expressed $\overline{C}_t = \overline{C} - \overline{C}_n$, Eq. (3) becomes

$$C = \overline{C} - \overline{C}_n + \overline{C}'_n = \overline{C} + (\overline{C}' - \overline{C})_n$$

or, using Eq. (4),

$$C = \overline{C} + (\overline{C}_r)_n. \tag{5}$$

Here $(\overline{C}_r)_n$ signifies the normal component of the relative velocity. In a similar way from Eqs. (3) and (4):

$$\begin{aligned} C' &= \overline{C}'_t + \overline{C}_n = \overline{C}'_t + (\overline{C}_n - \overline{C}'_n) + \overline{C}'_n \\ &= \overline{C}'_t + \overline{C}'_n - (\overline{C}_r)_n, \end{aligned}$$

and since $\overline{C}'_t + \overline{C}'_n = \overline{C}'$,

$$C' = \overline{C}' - (\overline{C}_r)_n. \tag{6}$$

Equations (5) and (6) may be written in terms of their components along the three coordinate axes. Call the components of the velocity C, u, v, and w, and similarly for the other velocities, adding the proper subscripts. Furthermore, call the direction cosines of $(\overline{C}_r)_n$ the normal component of the relative velocity (this is, the same as the direction of the line of centers), l, m, n. Then according to Eq. (5)

$$\left.\begin{aligned} u &= \bar{u} + l \cdot (\overline{C}_r)_n \\ v &= \bar{v} + m \cdot (\overline{C}_r)_n \\ w &= \bar{w} + n \cdot (\overline{C}_r)_n \end{aligned}\right\}, \tag{7}$$

and according to Eq. (6)

$$\left.\begin{aligned} u' &= \bar{u}' - l \cdot (\overline{C}_r)_n \\ v' &= \bar{v}' - m \cdot (\overline{C}_r)_n \\ w' &= \bar{w}' - n \cdot (\overline{C}_r)_n \end{aligned}\right\}. \tag{8}$$

Again, according to the definition of the relative velocity C_r the direction cosines of the normal component of the latter are

$$l = \frac{u' - u}{(\overline{C}_r)_n},\ m = \frac{v' - v}{(\overline{C}_r)_n},\ n = \frac{w' - w}{(\overline{C}_r)_n}.$$

Multiplying these equations in sequence by l, m, and n, the result is, since $l^2 + m^2 + n^2 = 1$,

$$(\overline{C}_r)_n = (\bar{u}' - \bar{u})l + (\bar{v}' - \bar{v})m + (\bar{w}' - \bar{w})n. \tag{9}$$

Putting these into Eqs. (7) and (8) the results are:

$$\left.\begin{aligned} u &= \bar{u} + \{l^2(\bar{u}' - \bar{u}) + lm(\bar{v}' - \bar{v}) + ln(\bar{w}' - \bar{w}) \\ v &= \bar{v} + \{lm(\bar{u}' - \bar{u}) + m^2(\bar{v}' - \bar{v}) + mn(\bar{w}' - \bar{w}) \\ w &= \bar{w} + \{ln(\bar{u}' - \bar{u}) + mn(\bar{v}' - \bar{v}) + n^2(\bar{w}' - \bar{w}) \end{aligned}\right\} \tag{10}$$

and

$$\left.\begin{aligned} u' &= \bar{u}' + \{l^2(\bar{u} - \bar{u}') + lm(\bar{v} - \bar{v}') + ln(\bar{w} - \bar{w}') \\ v' &= \bar{v}' + \{lm(\bar{u} - \bar{u}') + m^2(\bar{v} - \bar{v}') + mn(\bar{w} - \bar{w}') \\ w' &= \bar{w}' + \{ln(\bar{u} - \bar{u}') + mn(\bar{v} - \bar{v}') + n^2(\bar{w} - \bar{w}') \end{aligned}\right\}. \tag{11}$$

These expressions give the components of velocity uvw and $u'v'w'$ before the impact in terms of $\bar{u}\bar{v}\bar{w}$ and $\bar{u}'\bar{v}'\bar{w}'$ after impact, and *vice versa*.

29. Continuation of the Boltzman Derivation of the Distribution Law.—The equations deduced from the velocity exchanges in elastic impacts make it possible to calculate at once the desired velocity components before the impact. It must, however, be remembered that the quantities which it is required to find and which were expressed by $\bar{u}\bar{v}\bar{w}$ and $\bar{u}'\bar{v}'\bar{w}'$ in the first part of this deduction correspond to the quantities uvw and $u'v'w'$ of the section on Velocity Exchanges. Thus the quantities that have dashes over them in the *velocity exchange deduction* become the undashed quantities in this case, and *vice versa*. For example, according to Eq. (10) of the preceding section, for the velocity components $\bar{u}\bar{v}\bar{w}$ of the molecules which after impact will fall into type A, the following values are found:

$$\bar{u} = u - \{l^2(u - u') + lm(v - v') + ln(w - w')\}.$$
$$\bar{v} = v - \{lm(u - u') + m^2(v - v') + mn(w - w')\}.$$
$$\bar{w} = w - \{ln(u - u') + mn(v - v') + n^2(w - w')\}.$$

And for the velocity components $\bar{u}'\bar{v}'\bar{w}'$ of the molecules which after impact will belong to the B type of molecules, from Eq. (11) of the preceding section the following values are found:

$$\bar{u}' = u' - \{l^2(u' - u) + lm(v' - v) + ln(w' - w)\}.$$
$$\bar{v}' = v' - \{lm(u' - u) + m^2(v' - v) + mn(w' - w)\}.$$
$$\bar{w}' = w' - \{ln(u' - u) + nm(v' - v) + n^2(w' - w)\}.$$

From analogy to the considerations for the number of impacts in dt which removed A-type molecules from the class by α impacts the number of impacts between these molecules *leading to the formation of A and B molecules* per unit volume in dt is given by $F(\bar{u}\bar{v}\bar{w})F(\bar{u}'\bar{v}'\bar{w}')(\delta^2 c_r \cos\theta dK d\bar{u} d\bar{v} d\bar{w} d\bar{u}' d\bar{v}' d\bar{w}' dt)$. This expression is the exact analogue of the previous expression for the disappearance of A molecules, and may be written

$$\overline{FF'}\delta^2 c_r \cos\theta dK d\bar{u} d\bar{v} d\bar{w} d\bar{u}' d\bar{v}' d\bar{w}' dt.$$

These are, however, not necessarily β impacts but can only be so if the quantities $d\bar{u}$, $d\bar{v}$, $d\bar{w}$, $d\bar{u}'d\bar{v}'d\bar{w}'$ are so determined that $\bar{u} + d\bar{u}$, etc., *before* the impact go over into $u + du$, etc. *after* the impact, for a β impact is so defined that the molecule must go into the A type (having velocities between u and $u + du$, etc.) *after* the impact—that is, not only must $\bar{u}\bar{v}\bar{w}$ go over into u, v, and w after the impact, but $\bar{u} + d\bar{u}$, $\bar{v} + d\bar{v}$, and $\bar{w} + d\bar{w}$ must go

over into $u + du$, $v + dv$, and $w + dw$. In order that this may occur, $d\bar{u}$, $d\bar{v}$, $d\bar{w}$, $d\bar{u}'$, $d\bar{v}'$, $d\bar{w}'$ must be so determined that they correspond to the quantities du, dv, dw, du', dv', dw' after impact. The quantities $d\bar{u}$, . . . $d\bar{w}'$ must be determined by differentiation of the equations giving $\bar{u}$, . . . $\bar{w}'$ in terms of u, . . . w' above. Differentiating thus,

$$d\bar{u}d\bar{v}d\bar{w} \cdot d\bar{u}'d\bar{v}'d\bar{w}' = \Delta dudvdw \cdot du'dv'dw'$$

is obtained, where Δ is the substitution determinant.

$$\Delta = \begin{vmatrix} \frac{\partial \bar{u}}{\partial u}, & \frac{\partial \bar{u}}{\partial v}, & \frac{\partial \bar{u}}{\partial w}, & \frac{\partial \bar{u}}{\partial u'}, & \frac{\partial \bar{u}}{\partial v'}, & \frac{\partial \bar{u}}{\partial w'} \\ \frac{\partial \bar{v}}{\partial u} & & & & & \frac{\partial \bar{v}}{\partial w'} \\ \frac{\partial \bar{w}}{\partial u} & & & & & \frac{\partial \bar{w}}{\partial w'} \\ \frac{\partial \bar{u}'}{\partial u} & & & & & \frac{\partial \bar{u}'}{\partial w'} \\ \frac{\partial \bar{v}'}{\partial u} & & & & & \frac{\partial \bar{v}'}{\partial w'} \\ \frac{\partial \bar{w}'}{\partial u} & & & & & \frac{\partial \bar{w}'}{\partial w'} \end{vmatrix}.$$

The coefficients of these come from the equations for $\bar{u}\bar{u}\bar{w}$ and $\bar{u}'\bar{v}'\bar{w}'$ and it is seen that Δ is given by

$$\Delta = \begin{vmatrix} 1 - l^2, & -lm, & -ln, & l^2, & lm, & ln \\ -lm, & 1 - m^2, & -mn, & lm, & m^2, & mn \\ -ln, & -mn, & 1 - n^2, & ln, & mn, & n^2 \\ l^2, & lm, & ln, & 1 - l^2, & -lm, & -ln \\ lm, & m^2, & mn, & -lm, & 1 - m^2, & -mn \\ ln, & mn, & n^2, & -ln, & -mn, & 1 - n^2 \end{vmatrix}.$$

Evaluation of this determinant yields the result that $\Delta = +1$. Hence $d\bar{u}d\bar{v}d\bar{w} \cdot d\bar{u}'d\bar{v}'d\bar{w}' = dudvdw \cdot du'dv'dw'$. This equation is a special case of a famous theorem of Liouville. It is therefore found that if the velocity vectors of two molecules before an impact be in definite volume elements of the velocity space, they will after impact lie in different volume elements, which, however, are of the same size as the initial elements.

Thus the equation for the formation of A molecules from β impacts takes on the form

$$\bar{F}\bar{F}'\delta^2 c_r \cos \theta dK dudvdw \cdot du'dv'dw' \cdot dt.$$

The net increase of the A-type molecules in unit volume through impacts of the α and β type in the time dt is, therefore,

$$(\bar{F}\bar{F}' - FF')\delta^2 c_r \cos\theta dK du dv dw du' dv' dw' \cdot dt.$$

By integration over all values of $u'v'w'$ as well as all values of dK, the increase in the number of A molecules in unit volume in the time dt through all possible impacts, is obtained, to wit

$$du dv dw \cdot dt \int\int\int\int (\bar{F}\bar{F}' - FF')\delta^2 c_r \cos\theta dK du' dv' dw'.$$

Now the number of molecules of type A was assumed to be $F(uvw)du dv dw$ at the beginning of the discussion. This number in the time dt changes to

$$\left(F + \frac{\partial F}{\partial t} dt\right) du dv dw.$$

Hence the increase in the number of A-type molecules per unit volume in a time dt is expressed by,

$$\frac{\partial F}{\partial t} dt \cdot du dv dw.$$

Accordingly,

$$\frac{\partial F}{\partial t} = \int\int\int\int (\bar{F}\bar{F}' - FF')\delta^2 \cdot c_r \cos\theta \cdot du' dv' dw' dK.$$

From this equation it follows that the relation

$$\bar{F}\bar{F}' - FF' = 0$$

is a *sufficient* condition that $\partial F/\partial t = 0$, that is to say, it is a sufficient condition that a stationary state has been reached. It does not prove that it is a necessary condition, for in order to make $dF/dt = 0$ it is only necessary that the integral as a whole vanish. This will occur if $\bar{F}\bar{F}' - FF'$ is equal to 0. It will also occur if the quantity $\bar{F}\bar{F}' - FF'$ has *positive* and *negative* values such that the integration carried out between the limits makes the integral vanish. If it could be shown that $\bar{F}\bar{F}' - FF'$ is always positive or always negative, the condition $\bar{F}\bar{F}' - FF' = 0$ would be both a sufficient and a necessary condition that the integral vanish.

The condition, however, that $\partial F/\partial t = 0$ is sufficient to determine the distribution law. If it is brought to vanish through $\bar{F}\bar{F}' - FF'$ being zero, the distribution law evaluated by this condition would be a possible distribution law. In order to

show that it is the *only* distribution law, the condition that $\overline{F}\overline{F}' - FF' = 0$ would have to be proved to be the *necessary* and *sufficient* condition for $\partial F/\partial t$ becoming 0. This was accomplished by Boltzmann by means of his famous H theorem.

30. Application of the H Function.—To prove that $\overline{F}\overline{F}' - FF'$ is always of one sign in the integration, Boltzmann studied the so-called H function, or logarithmic function,

$$H = \int\int\int F \log F du dv dw,$$

in which the integration is to be carried out over all possible values of u, v, and w, *i.e.*, from $-\infty$ to $+\infty$. H is thus a pure number entirely independent of u, v, and w, and dependent only on the analytic form of F. Now in equilibrium F is not supposed to change with time, that is, the function represented by F is the one expressing the equilibrium condition. Thus the condition of equilibrium may be expressed by writing that $dH/dt = 0$, for if F is a constant with respect to time the derivative of $\int\int\int F \log F du dv dw$ with respect to t must be 0.

It is next necessary to determine dH/dt relative to the quantities which have been dealt with. Differentiating $F \log F du dv dw$ under the integral sign,

$$\frac{dH}{dt} = \int\int\int\left(\frac{dF}{dt} + \frac{dF}{dt}\log F\right) du dv dw.$$

Putting in the value of dF/dt obtained for the increase in A molecules above the expression

$$\frac{dH}{dt} = \int\int\int\int\int\int\int(1 + \log F)\,(\overline{F}\overline{F}' - FF')\delta^2 c_r \cos\theta du \ldots dw' dK$$

is obtained. Now so far the A molecules only have been emphasized, inasmuch as it was desired to determine their increase in number. Actually, the B molecules also change, and since the B molecules are in no way subordinate to A molecules in these processes their changes must be included in the calculations. In fact, the division of molecules into A and B types was, in reality, only a mathematical convenience for simplifying the discussion. Thus there must exist for the B molecules a set of equations analogous to those for the A molecules in which the

accented letters are merely substituted for the unaccented letters, to wit

$$\frac{\partial F'}{\partial t} = \int\int\int\int (FF' - FF'')\delta^2 c_r \cos\theta du dv dw dK$$

and

$$H = \int\int\int F' \log F' du' dv' dw'.$$

These two lead to an equally justified value for dH/dt, namely,

$$\frac{dH}{dt} = \int\int\int\int\int\int\int (1 + \log F') (FF' - FF'')\delta^2 c_r \cos\theta du \ldots dw' dK.$$

Addition of these two expressions for dH/dt and division by 2 lead to an average value for dH/dt, in which both collisions are equally regarded. This value takes the form

$$\frac{dH}{dt} = \frac{1}{2}\int\int\int\int\int\int\int (2 + \log FF') (FF' - FF'')$$
$$\delta^2 c_r \cos\theta du \ldots dw' dK.$$

This value again, however, considers only the α type of impacts, since the α type of impacts was taken as the starting point of the discussion. Since the β collisions could have been used as the starting point as well as the α, they must be included in the evaluation of a final neutral value of dH/dt. Thus two expressions can be gained analogous to those just averaged which would follow if the β impacts had been used as the starting point. These are obtained again by merely interchanging the dashed and undashed letters for dF/dt and dF'/dt used before and for the H used before. If this transformation is carried out, the effect of the use of the β type of impacts as a starting point leads to the expression

$$\frac{dH}{dt} = -\frac{1}{2}\int\int\int\int\int\int\int (2 + \log \bar{F}\bar{F}') (\bar{F}\bar{F}' - FF')\delta^2 c_r$$
$$\cos\theta du \ldots dw' dK,$$

in which, because of the relation $du \ldots dw' = du \ldots dw'$ the dashes were left off in the final differential product. Averaging this expression for dH/dt with the one based on the α impacts as a starting point, the perfectly symmetrical expression for dH/dt below is obtained:

$$\frac{dH}{dt} = \frac{1}{4}\int\int\int\int\int\int\int (\log FF' - \log \bar{F}\bar{F}') (\bar{F}\bar{F}' - FF')\delta^2 c_r$$
$$\cos\theta du \ldots dw' dK.$$

This integrand is always negative since $\overline{F}\overline{F}' - FF'$ has the opposite sign from $\log FF'/\overline{F}\overline{F}'$, while all other quantities are positive, for θ is always less than $\frac{\pi}{2}$. Since the integrand is always negative or equal to zero, integration between no limits whatever can make the integral vanish. Thus the integral can be 0 only if the integrand $\overline{F}\overline{F}' - FF'$ is 0.

31. Conclusion of Boltzmann's Method.—Since, therefore, the condition that $dH/dt = 0$ is synonymous with the state of equilibrium, equilibrium will occur *only* when

$$\overline{F}\overline{F}' - FF' = 0.$$

This condition is, accordingly, also the necessary condition for equilibrium. Thus the equilibrium condition is defined by $\overline{F}\overline{F}' - FF' = 0$ and by its means the form of the distribution law may be determined.

To arrive at this from the above equation it is simpler to divide the equation by N, the number of molecules per unit volume, and one has the equation in the form,

$$\bar{f}\bar{f}' - ff' = 0, \text{ where } \bar{f}, \bar{f}', f, f' \text{ express } \frac{\overline{F}}{N}, \frac{\overline{F}'}{N}, \frac{F}{N}, \frac{F'}{N}.$$

Furthermore, since for equilibrium all directions in space are equivalent, therefore the f's depend on the magnitudes *of the velocities only* and not on the directions. This may be expressed by the equations

$$\begin{aligned} f &= e^{\phi(c^2)} \\ f' &= e^{\phi(c'^2)} \\ \bar{f} &= e^{\phi(\bar{c}^2)} \\ \bar{f}' &= e^{\phi(\bar{c}'^2)}, \end{aligned}$$

for the letter c represents the appropriate vector velocities of the molecules in the A, B, α, and β impact classes. The square is used to make them independent of the sign of the velocity. From the law of conservation of energy one can write

$$c^2 + c'^2 = \bar{c}^2 + \bar{c}'^2$$

hence

$$\bar{c}^2 = c^2 + c'^2 - \bar{c}'^2.$$

Putting $\bar{f}\bar{f}' - ff' = 0$ into logarithmic form

$$\log \bar{f} + \log \bar{f}' - \log f - \log f' = 0,$$

and substituting the values for $\bar{f}, \bar{f}', f$ and f' assumed above, one obtains

$$\phi(\bar{c}^2) + \phi(\bar{c}'^2) - \phi(c^2) - \phi(c'^2) = 0.$$

Substituting for $\bar{c}^2$, this becomes $\phi(c^2) + \phi(c'^2) = \phi(\bar{c}'^2) + \phi(c^2 + c'^2 - \bar{c}'^2)$.

Differentiating this partially with respect to c^2, c'^2, and $\bar{c}'^2$ respectively, one obtains

$$\phi'(c^2) = \phi'(c^2 + c'^2 - \bar{c}'^2)$$
$$\phi'(c'^2) = \phi'(c^2 + c'^2 - \bar{c}'^2)$$
$$\phi'(\bar{c}'^2) = \phi'(c^2 + c'^2 - \bar{c}'^2)$$

or

$$\phi'(c^2) = \phi'(c'^2) = \phi'(\bar{c}'^2).$$

Such an equation can hold only if the derivatives are equal to a constant which one may call $-1/\alpha^2$, *i.e.*, if

$$\phi'(c^2) = -\frac{1}{\alpha^2}.$$

Integrating this and calling $\log A^3$ a constant of integration,

$$\phi(c^2) = -\frac{1}{\alpha^2}c^2 + \log A^3,$$

that is, it can hold only if

$$f = e^{\phi(c^2)} = A^3 e^{-\frac{c^2}{\alpha^2}}.$$

But f is the abbreviation of $f(u, v, w)$, and $c^2 = u^2 + v^2 + w^2$, so that

$$f(u, v, w) = A^3 e^{-\frac{1}{\alpha^2}(u^2+v^2+w^2)}$$

or, separately, $f(u) = Ae^{-\frac{u^2}{\alpha^2}}$, $f(v) = Ae^{-\frac{v^2}{\alpha^2}}$, and $f(w) = Ae^{-\frac{w^2}{\alpha^2}}$. If there are N molecules present in a cm³ the numbers having velocities between u and $u + du$, v and $v + dv$, and w and $w + dw$ are given by $N_{du} = Nf(u)du = ANe^{-\frac{u^2}{\alpha^2}}du$, $N_{dv} = ANe^{-\frac{v^2}{\alpha^2}}dv$, and $N_{dw} = ANe^{-\frac{w^2}{\alpha^2}}dw$.

This is the expression indicating the distribution of velocities. The physical meaning of the constants A and α will be determined in the treatment of the distribution law as deduced by Maxwell (Secs. 34 and 35).

32. The H Theorem and the Meaning of H.—The significance of the quantity H is far more extensive than a mere aid to the determination of the distribution law, for it makes it possible to obtain a mechanical significance for an otherwise difficultly interpretable quantity, namely, the entropy. It is, however, beyond the scope of this text to derive the relationship or to enter into the more recent rigorous proofs of the H theorem. This falls into the domain of statistical mechanics.

It was noticed that the integrand in the expression for dH/dt was always negative and in the limiting case of equilibrium 0. Thus for every case deviating from the stationary state one obtains the inequality

$$\frac{dH}{dt} < 0$$

and *only* for the stationary state does one obtain the equation $dH/dt = 0$. These two statements constitute the Boltzmann H theorem in its simplest form. Its significance consists in the following:

Thermodynamics teaches that an isolated system can successively take on only such states that its entropy always increases. If the entropy can no longer increase the system remains in a state of equilibrium which is defined by this fact. Thus entropy as a function of time follows the inequality that $dS/dt \geqq 0$; the negative entropy will consequently be represented by the relation $-dS/dt \leqq 0$, which is completely analogous to the inequality for H. Thus it is expected that H must be closely related to negative entropy. Since H has a purely mechanical definition, a mechanical definition of entropy is reached. In fact, it can be shown by analysis that for a monatomic gas in equilibrium the entropy, aside from certain constants of integration, is related to the quantity H by the relation

$$S = -\frac{R}{N_A}H,$$

where R is the universal gas constant and N_A is the Avogadro number. A still further analysis leads to the interesting result that H is the negative logarithm of the thermodynamic probability. This thermodynamic probability is, in turn, the number of equally probable configuration of the states of the separate molecules which will give a resultant thermodynamic state in the gas. Thus the negative logarithm of the chance that the separate molecules will find themselves in such a configuration of states as to give a certain thermodynamic state in the gas is the quantity H. From the relation between H and entropy one can then write that, since $-\log W_{therm.} = H$, therefore $S = R/N_A \log W_{therm.}$ Here $W_{therm.}$ signifies the thermodynamic probability.

33. Maxwell's Deduction of the Distribution of Velocities.— The law which was deduced by Boltzmann from a study of the equilibrium state existing among the molecules making elastic

impacts was originally deduced by Maxwell from considerations of pure probabilities. It happens that the assumptions which must be made concerning the behavior of the molecules fall into a general set of conditions in the theory of probabilities which at once specify the form of the distribution law.* These conditions are so general that no specific applications to molecules need be made, only the molecules must be assumed to fulfil certain conditions. These conditions imply that a steady state has been reached and no remnants of external disturbances exist in the gas. It also requires that enough molecules be considered so that deviations from a mean condition throughout the gas are highly improbable. What really should be shown and must exist, as the conditions give the true distribution law is that the equilibrium resulting from elastic impacts fulfils the conditions imposed in the derivation.

Let the gas molecules be assumed to obey the following conditions.

1. Assume equilibrium with enough molecules so that the number of molecules in any region is the same and so that the velocities in any direction are equal. In other words, assume that the numbers considered are great enough so that in any volume of the gas there will be equal numbers of molecules and that the molecules will have the same velocities in all directions. The assumption also demands that no clumping or aggregation of the molecules exists and that all convection or mass movements in the gas be absent. These assumptions lead to the following consequences:

a. The components of velocity along any system of coordinates are equal.

b. This isotropy of the gas makes it immaterial what coordinate system the results are expressed in. In other words, an equating of the functions expressed in different coordinate systems would amount to a statement of the isotropy of the gas.

* Maxwell's original proof is, however, not a definite proof of the conditions existing among the molecules as pointed out by Boltzmann. "On the one hand, the distribution of velocities in a stationary state is called forth by impacts. On the other hand, in the deduction which follows the existence of impacts does not enter in at any point, for no use is made of the laws of impact. This proof then, if it be assumed correct, could be used to show that Maxwell's law holds if no impacts took place, a thing which is impossible. A rigorous proof of the law can then only come from a study of the impacts."

2. The velocities along any three coordinate axes are independent of each other. A statement of this independence would be included in multiplying the chance of a velocity along any one axis, which depends on the velocity only, with the chance of the velocity along one of the other axes and stating that the resultant chance is the chance of a combined velocity containing the two components, for the multiplication of two probabilities to give the resultant probability can only occur if the probabilities are independent phenomena.*

3. Assume the freedom of velocity distribution from any other influences, that is, assume that the chance of the velocity of a molecule lying between certain limits is a function of the *velocity considered and of the limits only*. This is the same as asserting that the distribution of molecular velocities can be represented by a probability function and is similar to the assumption made in deducing the distribution of the free paths.

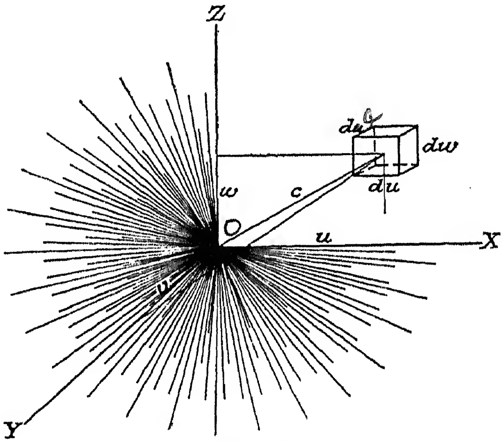

FIG. 18.

Having laid down the assumptions concerned, it is next convenient to visualize the molecular velocities in the following manner:

Assume that at a given instant all the velocities of the molecules in a volume of gas could be photographed as vectors whose lengths give the magnitude and whose directions are the directions of all the molecular motions at that time. These vectors could then be arranged so that they all started from a common origin *O*. If this were done, the resulting figure in space would resemble a perfectly symmetrical spiny sea urchin radiating from the center *O*. Such a figure is represented in Fig. 18. The

* This assumption is not at once obvious, for actually among the molecules the components of velocity along any three coordinate axes u, v, and w are subject to certain relations, to wit, the conservation of momenta and of energy in the case of real molecules. It, however, happens that the laws of impact so affect the relations that the conditions are fulfilled and the deduction accordingly leads to the correct result.

spines would have varying lengths, there being a few very long ones and a few short ones, with the length of most of them lying about a certain mean value. If about O the two spheres be drawn of radii c and $c + dc$, the vectors ending between these two would constitute all the velocities present that had values lying between c and $c + dc$.

Now let O be chosen as the origin of any rectangular system of coordinates x, y, z. Then any given velocity vector c could be decomposed into components u, v, and w along x, y, and z. Thus the relation $c^2 = u^2 + v^2 + w^2$ may be assumed to apply between the components and c.

From assumption 3 it can be stated that the chance that an x velocity component ends between u and $u + du$ is purely a function of the values of u and du, *i.e.*, it may be written $f(u)du$. Since the velocities are similar and equivalent (assumption 1*a*) in all directions, the chance of a velocity component along y having values between v and $v + dv$ and one along z of having values between w and $w + dw$ is expressed as $f(v)dv$ and $f(w)dw$ respectively. The chance that a velocity vector ends simultaneously between u and $u + du$, v and $v + dv$, and w and $w + dw$ is, from assumption 2, given by the product

$$f(u)f(v)f(w)dudvdw.$$

This same group of coordinates goes to make up a single vector c as stated above. The chance that this single velocity of value c ends in the volume element $dudvdw$ is then, by assumption 3, a function of c and of $dudvdw$ only. That chance may be expressed as $F(c)dudvdw$, following the notation above. For convenience, it may just as well be written as $\phi(c^2)\,dudvdw$, where ϕ represents the appropriate form of the function. It now becomes possible to express the independence of coordinate systems assumed in 1 b. in the form

$$f(u)f(v)f(w)dudvdw = \phi(c^2)dudvdw,$$

or

$$f(u)f(v)f(w) = \phi(u^2 + v^2 + w^2).$$

This condition at once determines the form of the distribution law, for it equates the product of a set of functions to a function of the sum of the variables. Such a relation is indicative of a logarithmic relationship between the variables. Maxwell goes at once to the law from the implication contained in this. It is, however, possible to deduce this relation mathematically from the above equation.

For the particular value of c chosen, $\phi(c^2)$ is a constant, that is, the differential of this quantity is equal to 0, hence $d[\phi(c^2)] = 0 = d[f(u)f(v)f(w)]$. Differentiating,

$$f'(u)f(v)f(w)du + f(u)\, f'(v)f(w)dv + f'(w)f(u)f(v)dw = 0,$$

where the symbol $f'(u)$ represents the derivative of $f(u)$ etc. Dividing by $f(u)\, f(v)\, f(w)$ the equation becomes

$$\frac{f'(u)}{f(u)}\, du + \frac{f'(v)}{f(v)}\, dv + \frac{f'(w)}{f(w)}\, dw = 0.$$

Now $c^2 = u^2 + v^2 + w^2$, hence as c is a constant $udu + vdv + wdw = 0$. Multiplying this by a constant λ and adding the resultant to the equation for the ratio of the derivative of the function to the functions

$$\left(\frac{f'(u)}{f(u)} + \lambda u\right) du + \left(\frac{f'(v)}{f(v)} + \lambda v\right) dv + \left(\frac{f'(w)}{f(w)} + \lambda w\right) dw = 0$$

is obtained.

Since by assumption 2 the velocity components are independent of each other this equation can be 0 only if each one of the terms separately is equal to 0. This can be expressed by the equations below:

$$\frac{f'(u)}{f(u)}\, du = -\lambda u du, \text{ or } \log f(u) = -\frac{\lambda}{2} u^2 + \log A.$$

$$\frac{f'(v)}{f(v)}\, dv = -\lambda v dv, \text{ or } \log f(v) = -\frac{\lambda}{2} v^2 + \log A.$$

$$\frac{f'(w)}{f(w)}\, dw = -\lambda w dw, \text{ or } \log f(w) = -\frac{\lambda}{2} w^2 + \log A.$$

Here A is a constant of integration to be determined later. From these equations it follows that

$$f(u) = Ae^{-\frac{\lambda}{2} u^2}.$$

$$f(v) = Ae^{-\frac{\lambda}{2} v^2}.$$

$$f(w) = Ae^{-\frac{\lambda}{2} w^2}.$$

Call $\frac{\lambda}{2} = \frac{1}{\alpha^2}$.

Thus $f(u)du$, the chance that a molecule has the velocity between u and $u + du$, is given by

$$f(u)du = Ae^{-\frac{u^2}{\alpha^2}}\, du.$$

If there are N molecules present in a cm³ the number having velocities of this value is given by

$$N_{du} = NAe^{-\frac{u^2}{\alpha^2}}du \text{ and likewise for } v \text{ and } w.$$

$$N_{dv} = NAe^{-\frac{v^2}{\alpha^2}}dv.$$

$$N_{dw} = NAe^{-\frac{w^2}{\alpha^2}}dw.$$

This is the same equation as was obtained in Boltzman's deduction above.

34. Evaluation of Constants A, and α of Boltzmann and Maxwell's Deductions.—It now remains to determine the constants A and α. This is done as follows:

$$N = \int_{-\infty}^{+\infty} N_{du},$$

hence

$$N = AN\int_{-\infty}^{+\infty} e^{-\frac{u^2}{\alpha^2}}du.$$

This is a definite integral whose values is $\frac{2}{2\frac{1}{\alpha}}\sqrt{\pi}$.

Therefore

$$1 = A\alpha\sqrt{\pi}$$

or

$$A = \frac{1}{\alpha\sqrt{\pi}}.$$

$$N_{du} = N\frac{1}{\alpha\sqrt{\pi}}e^{-\frac{u^2}{\alpha^2}}du$$

$$N_{dv} = N\frac{1}{\alpha\sqrt{\pi}}e^{-\frac{v^2}{\alpha^2}}dv$$

$$N_{dw} = N\frac{1}{\alpha\sqrt{\pi}}e^{-\frac{w^2}{\alpha^2}}dw$$

and

$$f(u) = \frac{1}{\alpha\sqrt{\pi}}e^{-\frac{u^2}{\alpha^2}}.$$

$$f(v) = \frac{1}{\alpha\sqrt{\pi}}e^{-\frac{v^2}{\alpha^2}}.$$

$$f(w) = \frac{1}{\alpha\sqrt{\pi}}e^{-\frac{w^2}{\alpha^2}}.$$

The chance of a velocity ending simultaneously between u and $u + du$, v and $v + dv$, and w and $w + dw$ is then

$$f(u)f(v)f(w)dudvdw = \frac{1}{\alpha^3\pi^{3/2}}e^{-\frac{u^2+v^2+w^2}{\alpha^2}}dudvdw.$$

$c^2 = u^2 + v^2 + w^2$, and $dudvdw$ is given by $dc \times cd\theta \times c \sin \theta d\phi$ in Fig. 19. Hence

$$f(u)f(v)f(w)dudvdw = \frac{1}{\alpha^3\pi^{3/2}}e^{\frac{-c^2}{\alpha^2}}c^2dc \sin \theta d\theta d\phi.$$

This is the chance of the velocity ending in the element of volume $dudvdw$, or between c and $c + dc$, θ and $\theta + d\theta$, and ϕ and $\phi + d\phi$. To get the chance of a velocity ending between c and $c + dc$ this must be integrated for all values of θ from 0 to π and for ϕ from 0 to 2π, that is, it must be integrated all over the spherical shell of thickness dc lying between c and $c + dc$. If there are N molecules present in a cm^3, the number having velocities between c and $c + dc$ is obtained by multiplying the quantity

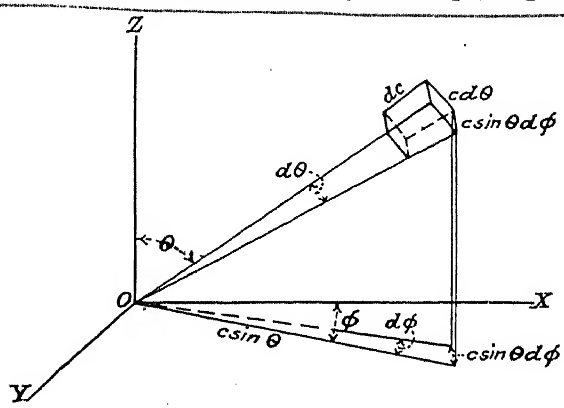

FIG. 19.

above by N and integrating over the limits mentioned. Hence

$$N_{dc} = \frac{N}{\alpha^3\pi^{3/2}} e^{-\frac{c^2}{\alpha^2}}c^2dc \int_0^{\pi}\int_0^{2\pi} \sin \theta d\theta d\phi$$
$$= \frac{4N}{\alpha^3\sqrt{\pi}} c^2e^{-\frac{c^2}{\alpha^2}} dc.$$

This same operation can be carried out more simply by writing

$$f(u)f(v)f(w) = \frac{1}{\pi^{3/2}\alpha^3} e^{-\frac{c^2}{\alpha^2}}.$$

The chance that this vector ends between c and $c + dc$ is then $f(u)f(v)f(w)$ times the volume between c and $c + dc$ in the spherical shell. This has a surface $4\pi c^2$ and is dc thick, and hence the chance of ending in dc is given by

$$P_{dc} = f(u)f(v)f(w)4\pi c^2dc$$
$$= \frac{4}{\alpha^3\sqrt{\pi}} c^2e^{-\frac{c^2}{\alpha^2}}dc.$$

If there are N molecules present in a cm^3 the number of vectors ending between c and $c + dc$ is

$$N_{dc} = \frac{4N}{\alpha^3\sqrt{\pi}} c^2 e^{-\frac{c^2}{\alpha^2}} dc.$$

The meaning of α may now be determined by considering the form of this function. Unlike the distribution of free paths, it is found that, at $c = 0$, $N_{dc} = 0$, and at $c = \infty$, $N_{dc} = 0$. In between the function is always positive, and hence it has a maximum. This maximum represents the speed for which N_{dc} is the greatest; that is to say, it is the *most probable speed.* To find this N_{dc} must be differentiated and equated to 0.

$$\frac{dN_{dc}}{dc} = 0 = -\frac{2c}{\alpha^2} e^{-\frac{c^2}{\alpha^2}} c^2 dc + e^{-\frac{c^2}{\alpha^2}} 2c\,dc,$$

whence

$$c = \alpha.$$

Hence the α of this equation represents *the most probable speed.*

35. Plot of the Law and Various Averages. It is now possible to plot the curve representing this law. For the purpose of plotting it is to be noted that the equation may be written in terms of the parameter $\frac{c}{\alpha}$, that is, the velocities may be expressed in terms of their values relative to α, the most probable speed, *i.e.*, relative to the maximum of the curve. Then to plot it one may write

$$N_{dc} = \frac{4}{\sqrt{\pi}} N \frac{c^2}{\alpha^2} e^{-\frac{c^2}{\alpha^2}} \frac{dc}{\alpha} = \frac{4N}{\sqrt{\pi}} x^2 e^{-x^2} dx, \text{ where } x = \frac{c}{\alpha}.$$

If, then, a suitable value for dx be chosen, say $dx = dc/\alpha = 0.10$, N_{dc} may be evaluated for various values of x. Such a plot is shown in Fig. 20, where N was chosen as 100.

It is seen at once that the curve is not symmetrical as regards $c = \alpha$, or $x = 1$. In fact, a slightly greater area lies to the right of $x = 1$. It is then obvious that α will not represent the average speed but will be less. Let the average speed $\bar{c}$ be computed

$$\bar{c} = \int_0^\infty \frac{cN_{dc}}{N} = \frac{1}{N}\int_0^\infty \frac{4N}{\alpha^3\sqrt{\pi}} e^{-\frac{c^2}{\alpha^2}} c^3 dc.$$

Putting it into terms of $c/\alpha = x$, $dc/\alpha = dx$,

$$\bar{c} = \frac{4\alpha}{\sqrt{\pi}}\int_0^\infty x^3 e^{-x^2} dx.$$

This, again, is a definite integral whose value leads to $\bar{c} = 2\alpha/\sqrt{\pi}$. Thus the average speed is $2/\sqrt{\pi}$ times the most probable speed, that is, $\bar{c} = 1.128\alpha$.

Finally, the dissymmetry of the curve demands the use of a third average velocity. The molecular velocities are found experimentally from the relation that

$$p = \frac{1}{3}nm\bar{c}^2, \text{ where } nm = \rho, \text{ hence } \sqrt{\bar{c}^2} = \sqrt{\frac{3p}{\rho}}.$$

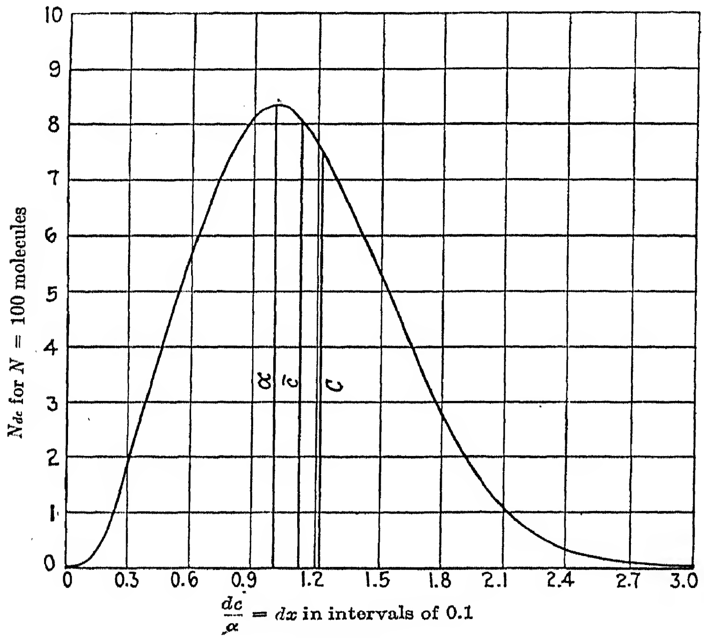

Fig. 20.

Thus the actual values of the velocities obtained *are not the average velocities* but the *square root of the average squared velocities* (Sec. 11). This, owing to the dissymmetry of the curve, will again be towards higher values of the velocity than either the most probable speed or the average speed, since in such an average the higher velocities will receive greater prominence. The root-mean-square speed, $\sqrt{\bar{c}^2}$, hereafter to be designated by C, is found as follows

$$C = \sqrt{\int_0^\infty \frac{c^2 N_{dc}}{N}} = \sqrt{\left[\frac{4}{\alpha^3\sqrt{\pi}}\int_0^\infty c^4 e^{-\frac{c^2}{\alpha^2}} dc\right]}$$

Putting $x = c/\alpha$,

$$C = \sqrt{\left| \frac{4\alpha^2}{\sqrt{\pi}} \int_0^\infty x^4 e^{-x^2} dx \right|} \text{ is obtained, whence}$$

$$C = \sqrt{\left| \frac{3\alpha^2}{2} \right|} = \sqrt{\frac{3}{2}}\,\alpha = 1.224\alpha.$$

Thus one has to remember that molecular speeds are designated in terms of three quantities—the most probable, the average, and the square root of the mean square speed—which are related to each other by the equation

$$\alpha : \bar{c} : C = 1 : \frac{2}{\sqrt{\pi}} : \sqrt{\frac{3}{2}} = 1 : 1.128 : 1.224.$$

The ratio of $\bar{c}$ to C is seen to be $\sqrt{\frac{8}{3\pi}}$, or 0.922. Owing to these differences great care must be used in applying the equations of the kinetic theory in order to insure the use of the proper average.

36. Maxwell's Distribution Law and the Theorem of Equipartition.—In Section (9) of Chapter II it was shown that if one assumed the kinetic interpretation of gaseous pressure, and the experimental justification of Avogadro's rule one was lead to the conclusion that the average translational kinetic energy of each gas in a mixture of gases in equilibrium was the same. This conclusion was there asserted to be one manifestation of a more general law known as the Maxwell-Boltzmann law of equipartition of energy. It was also stated in a foot note that the deduction of the pressure of a gas on the basis of simple kinetic theory assumptions in Section (5) contained another aspect of the same assumption in the postulate that the velocity of the gas molecules along any one of the sides of the rectangular box was the same.

Inasmuch as the purpose of the kinetic theory is to formulate mathematically the behavior of gases on the basis of Newtonian mechanics it would seem more fitting that the law of equipartition should be deduced as a consequence of the asumptions of the fundamental kinetic theory by logical mathematical processes, and then be used in predicting Avogadro's rule, rather than the reverse. It happens that the first rigorous attempts at such a deduction resulted from some of the analyses made in the process of the deduction of Maxwell's law of distribution of velocities by the Boltzmann method. Furthermore the Maxwell deduction of this law also contained the tacit assumptions of the law of

equipartition restricted to translational velocities in its fundamental postulates. Finally the application of the law of equipartition to the interpretation of many physical problems is made by the use of the distribution law in such a form that it expresses the law of equipartition of energy. Accordingly since the law of equipartition of energy is bound up so intimately with the law of distribution of velocities it seems fitting that a brief discussion of its derivation should occur at this point. The application of the theorem of equipartition to the study of specific heats and the limitations of the theorem may, however, be properly discussed in a later chapter.

Before proceeding with the discussion it may be well to point out that very few questions in the kinetic theory of gases have been the subject of so much controversy as the questions of the validity of the various attempted proofs of the theorem of equipartition. While in the earlier years the problem was treated from the point of view of elastic molecular impacts, it has in recent years been studied almost exclusively by the more general and powerful methods of statistical mechanics. Unfortunately, the study of this subject would furnish the material for a book in itself, and so cannot be discussed at this point. From the more elementary point of view a very good idea of the problem can be obtained from both the elastic-solid-impact analysis, and from the elementary analysis by means of statistical mechanics given in Clemens-Schaefers "Einführung in die Theoretische Physik," vol. 2, part I, pages 401–403, and Chap. X, page 418 and especially pages 450 and 458ff. This[20] does not contain a critical review of the subject. For this reference may be made to Jeans "Dynamical Theory of Gases," Chaps. III, IV, and V.[21] There is also a very exhaustive study of the problems of statistical mechanics in an article by P. and T. Ehrenfest[22] in "Encyclopèdie des Sciences Mathèmatiques," vol. IV, I, Paris, 1915, which contains further references to later literature and a comment by Borel.

Historically, the theorem of equipartition of energy of molecules in a system of varying masses was first enunciated by Waterston[23] in 1845. His proof, according to a footnote by Rayleigh, could hardly be accepted as valid, although at the time Rayleigh commented on the importance of the contribution. Maxwell,[24] in 1859, independently arrived at the same conclusions. In 1861, Boltzmann[25] again brought the question into prominence and

extended it to all degrees of freedom in equilibrium. The matter was again discussed by Maxwell in a paper in 1879. Since then the question has been variously attacked by many workers, including Lorentz, Gibbs,[25] Jeans, and others chiefly in the field of statistical mechanics. Jeans[26] in particular believed to have derived the theorem in a rigorous fashion. Other workers appear to be dissatisfied with his deduction, and at present it is difficult to judge the exact status of the question. The question hinges largely on the implications included in the postulates on the basis of which the particular deduction is made. The exact situation might be stated as follows: Mathematical proofs of the theorem of equipartition have been given which very nearly, if not completely, establish the theorem as a result of the underlying assumptions of the application of Newtonian mechanics to gases made up of moving particles as postulated by the kinetic theory. On the other hand, while the experimental evidence to some extent bore out the predictions of the theorem, it seemed to fall seriously short in many cases. The explanation of this failure of the equipartition theorem was interpreted in the light of the new quantum effects.[27] The significance of these effects seems to lie in a direction which points towards a failure of the Newtonian mechanics and the laws of electrodynamics under certain conditions. If this explanation is correct, the failure of the equipartition theorem may in some measure be led back to a failure of the molecules to obey the laws of Newtonian mechanics assumed in the deduction of the equipartition theorem. This type of departure from classical mechanics is to be seen in the case of the behavior of C_p[28] for H_2 at low pressures and is not related to the relativity modifications. The application of the quantum mechanics to these phenomena then, in reality, is not a modification but rather an extension of the theorem to cover the problems introduced by non-Newtonian mechanics in the sense above mentioned. Thus it may be asserted that to a limited extent experiment bears out the predictions of the theorem of equipartition, while it shows clearly that the underlying assumptions are not completely adequate to describe all phenomena. The result is that it at present seems futile to discuss much further the question of the adequacy of the proofs of the theorem when it is faced with the difficulties encountered in the quantum effects. Considering the evidence as a whole, it would be not far from correct to accept the theorem as proved for practi-

cal purposes to the extent that the observed quantum effects will permit it.

In what follows a brief deduction of the law of equipartition as applied to translational motions of the molecules will be given in a manner similar to that used by Boltzmann following from his proof of the distribution law. The treatment here given is taken from Clemens-Schaefer and is a direct consequence of one of the steps of the deduction of the distribution law as given in Sec. 31. Following the derivation, a brief discussion of this type of derivation will be given as laid down by Jeans.[21] Finally, the distribution law for translational velocities will be written in a form which includes the assumption of equipartition of energy. The law will then be written in other forms as deduced by Clemens-Schaefer from statistical mechanics for the case rotational energies and for the case where the energies in equilibrium may be in any form. The equipartition law written in these forms, even though not deduced, will be of service in later applications of the theorem of equipartition and distribution of energies among the molecules.

Deduction of the Law of Equipartition for Translational Energies in Gaseous Mixtures.—All quantities referring to one of the gases of a binary gaseous mixture may be designated by the subscript 1, and all those of the other gas by the subscript 2. Then it is possible to consider impacts of molecules of one of the gases with each other, impacts of the molecules of the other gas with each other, and impacts of molecules of the one gas with molecules of the other gas. Now in Sec. 31, in the Boltzmann deduction of the distribution law, it was shown that the distribution law is defined by the relation expressing equilibrium in the form:

$$\bar{F}\bar{F}' - FF' = 0.$$

This relation also contains a proof of the law of equipartition for the translational energies in a gas, as will be seen in what follows. The expression above may at once be carried over to the case for equilibrium in a gaseous mixture if the proper subscripts are added to the letters. Before writing these expressions, the above expression may be reduced to the form independent of the number of the molecules present by dividing by the number of molecules per cm^3, or N. This gives the expression in the form

$$\bar{f}\bar{f}' - ff' = 0.$$

Applying it now to the mixtures of the two gases, three equations, are obtained applying in turn to gas 1, gas 2, and to the mixture of the gases.

$$\bar{f}_1\bar{f}_1' - f_1f_1' = 0 \text{ gas 1.}$$
$$\bar{f}_2\bar{f}_2' - f_2f_2' = 0 \text{ gas 2.}$$
$$\bar{f}_2\bar{f}_1' - f_2f_1' = 0 \text{ gas 1 and gas 2.}$$

As in Sec. 32, the first two expressions lead to the distribution law with the proper subscripts added to the constant terms. These take the form

$$f_1 = A_1^3 e^{-\frac{1}{\alpha_1^2}(u^2+v^2+w^2)} \text{ and } f_2 = A_2^3 e^{-\frac{1}{\alpha_2^2}(u^2+v^2+w^2)},$$

where $A_1 = \dfrac{1}{\alpha_1\sqrt{\pi}}$ and $A_2 = \dfrac{1}{\alpha_2\sqrt{\pi}}$.

Accordingly,

$$f_1 = \frac{1}{\alpha_1^3\pi^{\frac{3}{2}}}e^{-\frac{u^2+v^2+w^2}{\alpha_1^2}} \quad \text{and} \quad f_2 = \frac{1}{\alpha_2^3\pi^{\frac{3}{2}}}e^{-\frac{u^2+v^2+w^2}{\alpha_2^2}}$$

which may also be directly related to the average squared velocities C_1^2 and C_2^2 by the relations found in Sec. 35. The third relation between the dashed and undashed letters and the accented and unaccented letters will then be expressions of the form above, in which the velocity vectors u, v, and w take on the designation appropriate to their type. Simple algebraic manipulations of these expressions lead to an expression between the $1/\alpha_1$ and $1/\alpha_2$, which, translated in terms of the averaged square velocities, give the simple relation

$$\frac{1}{2}m_1C_1^2 = \frac{1}{2}m_2C_2^2.$$

This is the same expression deduced from Avogadro's rule and the pressure relation in a gas in Sec. 9 and which states equipartition. Thus the theorem of equipartition has been proved for translational motion for the case of a gas, using the assumptions of elastic impacts only. The validity of such a proof lies only in the question as to whether the conditions implying equipartition were not contained in one of the postulates underlying the theory. This was, in fact, done in deducing the law of distribution of velocities in Maxwell's fashion, through the assumption of independence of velocity coordinates coupled with the other assumptions. The proof of equipartition in the Boltzmann treatment above is as correct as the assumptions underlying the derivation of the distribution law. According to Jeans,[21] the derivation of

Boltzmann is not much better off in regard to the implied assumptions than Maxwell's original distribution-law derivation was. In Boltzmann's case the proof included the assumption of independence of space and velocity coordinates instead of the independence of velocity components among themselves. The question of the distribution law has been discussed by Boltzman[29] and by Lorentz.[30] Burbury[21] questions the validity of this proof, but the doubt is not shared by Jeans. In any case, the proof here given is not necessarily very rigorous, and as it is specialized in its scope, recourse should, in general, best be had to the more complete proofs in statistical mechanics.

It is of use to consider certain modifications of the distribution law which express at the same time the law of equipartition of energy. These laws are deduced from statistical reasoning and will only be given here in brief. The Maxwell distribution law in the form given in Sec. 35, expressing equipartition for translational energies, may be transformed into a form frequently written and indicating an energy distribution rather than a velocity distribution. The equation given in Sec. 35 was

$$N_{dc} = \frac{4N}{\alpha^3\pi^{1/2}}e^{-\frac{c^2}{\alpha^2}}c^2dc.$$

The c^2 and α^2 may be multiplied by m, the mass of a molecule, and the c^3 and α^3 by $m^{3/2}$. The equation then becomes

$$N_{dc} = \frac{4Nm^{3/2}}{m^{3/2}\alpha^3\pi^{1/2}}c^2e^{-\frac{mc^2/2}{m\alpha^2/2}}dc.$$

Now it was shown in Sec. 5 that $\frac{1}{3}NmC^2 = RT$, and in Sec. 35 that $\alpha^2 = \frac{2}{3}C^2$, whence $\frac{1}{2}Nm\alpha^2 = RT$. If the gas constant, R per cm^3, divided by N, the number of molecules per cm^3, be called k, where k is the average energy taken to raise the temperature of one molecule 1°, then it is at once found that $\frac{1}{2}m\alpha^2 = kT$. But $\frac{1}{2}m\alpha^2$ is the most probable kinetic energy of the molecules. Thus $\frac{1}{2}m\alpha^2$ can be expressed in terms of temperature from the relation above. The constant k is called the Boltzmann constant. Putting this into the equation above the relation is had in the form

$$N_{dc} = 4\pi N\left(\frac{m}{2\pi kT}\right)^{3/2}c^2e^{-\frac{mc^2}{2kT}}dc.$$

Occasionally, it is found convenient to write the expression above in another form. Designating $1/2kT$ by the letter h, the equation becomes

$$N_{dc} = 4\pi N\left(\frac{hm}{\pi}\right)^{3/2} c^2 e^{-hmc^2} dc,$$

which is a form often used in the literature.

For the case of rotational equipartion the distribution of rotational energies is given by

$$N_{d\omega} = 4\pi N\left(\frac{I}{2\pi kT}\right)^{3/2} \omega^2 e^{-\frac{I\omega^2}{2kT}} d\omega,$$

where $N_{d\omega}$ is the number of molecules out of N that have angular velocities between ω and ω and $d\omega$, and I is the moment of inertia.

Another interesting case is the number of molecules out of N that find themselves at a height z above the earth in its gravitational field. In this case there is equilibrium between the molecules due to their translational heat motions and the gravitational potential of the earth. This law is expressed by

$$N_{dz} = NBe^{-\frac{mgz}{kT}} dz.$$

Here B is a constant and g is the constant of gravitation. In general, for molecules with kinetic and potential energies in equilibrium the equation may be expressed as follows:

$$N_{dE} = NDe^{-\frac{E}{kT}} dE.$$

Here N_{dE} are the number out of N molecules having a total energy, kinetic or potential, between E and $E + dE$, and D is a constant. The last two equations can be used to give the relative number of molecules in two energy states by merely taking the ratios for two values of z or E. In this case the constants are eliminated.

37. Correction of Mean-free-path Equation of Clausius for Distribution of Velocities.—In the preceding deduction for the mean free paths (Sec. 18), the velocity u of the molecules was supposed to be the same for all the molecules. Actually, u is not the same and the derivation must be corrected for this fact. In the Clausius deduction the relative velocity of approach between two molecules was set as

$$r^2 = u^2 + v^2 - 2uv\cos\phi,$$

where ϕ was the angle between the velocities. This was reduced

to $r = u\sqrt{2}\sqrt{1 - \cos\phi}$ on the assumption that $u = v$. As this is no longer the case, the value for $\bar{r}$, the average relative velocity which is given by

$$\bar{r} = \int_0^\pi \frac{r \sin\phi d\phi}{2}, \checkmark$$

becomes

$$\begin{aligned}\bar{r} &= \frac{1}{2}\int_0^\pi \sqrt{u^2 + v^2 - 2uv\cos\phi}\,\sin\phi d\phi \\ &= \frac{1}{6uv}\Big[(u^2 + v^2 - 2uv\cos\phi)^{3/2}\Big]_0^\pi \\ &= \frac{1}{6uv}\Big[-(u^2 + v^2 - 2uv)^{3/2} + (u^2 + v^2 + 2uv)^{3/2}\Big] \\ &= \frac{1}{6uv}\Big[-(u - v)^3 + (u + v)^3\Big].\end{aligned}$$

The value of $\bar{r}$ depends on whether $u > v$ or $v > u$, for if $u > v$, solution gives for $u > v$ a positive value for $u - v$ and hence $\bar{r} = \frac{3u^2 + v^2}{3u}$. If $v > u$, $(u - v)$ becomes negative, the signs are reversed and it is necessary to write $\bar{r} = \frac{3v^2 + u^2}{3v}$. Now in the preceding deduction of Clausius, u was equal to the average speed, or $u = \frac{2}{\sqrt{\pi}}\alpha$. $\bar{r}$, however, must be determined from the chance of a given u or v taken from the Maxwell law. This probability for v is $P_v = \frac{4}{\alpha^3\sqrt{\pi}} v^2 e^{-\frac{v^2}{\alpha^2}} dv$, and for u is $P_u = \frac{4}{\alpha^3\sqrt{\pi}} u^2 e^{-\frac{u^2}{\alpha^2}} du$. It is now necessary to average $\bar{r}$ for collisions between molecules of all possible velocities. Since $\bar{r}$ depends on both u and v and on their relative magnitudes, it is necessary to proceed as follows: First assume u constant and take into account the variation of v. Then $\bar{r}_u$ becomes

$$\bar{r}_u = \frac{4}{\alpha^3\sqrt{\pi}}\left[\int_0^u \frac{3u^2 + v^2}{3u} v^2 e^{-\frac{v^2}{\alpha^2}} dv + \int_u^\infty \frac{3v^2 + u^2}{3v} v^2 e^{-\frac{v^2}{\alpha^2}} dv\right].$$

The integration between 0 and u of the $\frac{3u^2 + v^2}{3u}$ term applies to values of $u > v$, and the integration from u to ∞ of the $\frac{3v^2 + u^2}{3v}$ term applies to values of $u < v$. The $\bar{r}_u$ is then the average r for all values of v. It must next be multiplied by the chance of a

velocity u and integrated from 0 to ∞ to take account of the variations in the velocity u. The tedious integration will not be carried out here, and the reader is referred to the integration as carried out in Winkelmann's "Handbuch."[1] Integration yields

$$\bar{r} = \frac{2\alpha\sqrt{2}}{\sqrt{\pi}}, \text{ or } \frac{r}{u} = \sqrt{2}.$$

Hence the relative velocity of the molecules to be used in the equation for the free paths is now $\sqrt{2}$ times the average velocity of a single molecule. In Clausius' derivation the value found was $\bar{r} = 4u/3$. Thus the Maxwellian distribution of velocities changes the value of the relative velocity from 1.33 to 1.41. The expression for the mean free path

$$L = \frac{1}{\frac{4}{3}\pi\sigma^2 N}$$

previously deduced now becomes

$$L = \frac{1}{\sqrt{2}\pi\sigma^2 N}.$$

38. The Mean Free Paths of Molecules in a Gas Composed of Molecules of Different Kinds.—When *one* gas molecule of diameter σ_1 in a gas composed of molecules of diameter σ_2 is considered the question arises as to which value of σ to use in the expression $L = 1/\sqrt{2}\pi\sigma^2 N$. A brief consideration of the elementary deduction will show that for this simple case the molecule of radius σ_1 will exclude in its path L the centers of all molecules σ_2 which lie closer than $\sigma_1/2 + \sigma_2/2$ from it, for a collision occurs whenever the centers approach within $\frac{\sigma_1 + \sigma_2}{2}$ of each other. Thus for this case it is only necessary to replace the σ of the equation for homogeneous molecules by a value $\sigma_a = (\sigma_1 + \sigma_2)/2$.

The above expression was, however, deduced on the assumption that all molecules of diameter σ_2 are at rest, and that only the one molecule of diameter σ_1 is in motion. If now all molecules are moving, that of diameter σ_1 may have a velocity $\bar{c}_1$ different from those of diameter σ_2, whose velocity may be called $\bar{c}_2$. This case may be reduced to the one above by considering all the σ_2 molecules at rest and the σ_1 molecule moving relatively to them with the *average* relative velocity. This was done for the case of all molecules having the *same* velocities in

Sec. 19 and for the case of all molecules having the same *average* velocities, assuming Maxwell's distribution in Sec. 37 of Chap. IV. In the former case the relative velocity was $\bar{r} = 4\bar{c}/3$, and in the latter case it was $\bar{r} = \sqrt{2}\bar{c}$, where $\bar{c}$ was the average velocity. In the present instance the σ_1 molecules have an average velocity $\bar{c}_1$ and the σ_2 molecules an average velocity $\bar{c}_2$. It becomes necessary to derive the expression for $\bar{r}$ for the case where the two velocities exist. For the case that the σ_2 molecules move at right angles to the σ_1 molecules the relative velocity will be $\sqrt{\bar{c}_1^2 + \bar{c}_2^2}$, for the relative velocity is the sum of the two velocity vectors at right angles to each other. Thus in this case $\bar{r}/c_1 = \sqrt{\bar{c}_1^2 + \bar{c}_2^2}/\bar{c}_1$. In the earlier deductions where the molecules were all supposed to have the same velocity $\bar{c}$, $\bar{r}/\bar{c} = 4/3$, and where Maxwell's distribution was assumed, the molecules having the same average velocity $\bar{c}$, the ratio was $\bar{r}/\bar{c} = \sqrt{2}$. These values, in turn, put the factors $4/3$ and the $\sqrt{2}$ in the denominator of the equation for L. Hence were the expression above the true one for the relative velocity considering a σ_1 molecule moving among σ_2 molecules, L_1 would become

$$L_1 = \frac{1}{\pi\sigma_a^2 N \dfrac{\sqrt{\bar{c}_1^2 + \bar{c}_2^2}}{\bar{c}_1}}.$$

For L_2, the mean free path of a σ_2 molecule moving among σ_1 molecules, the expression would be

$$L_2 = \frac{1}{\pi\sigma_a^2 N \dfrac{\sqrt{\bar{c}_1^2 + \bar{c}_2^2}}{\bar{c}_2}}.$$

It now happens that if the rigorous analysis be carried through assuming a Maxwellian distribution of velocities with average velocities $\bar{c}_1$ and $\bar{c}_2$ for the molecules, the integrations for the average relative velocities, assuming all angles of motion of σ_1 molecules and σ_2 molecules, yields a relative velocity $\bar{r} = \sqrt{\bar{c}_1^2 + \bar{c}_2^2}$. This, strangely, is the value found to be the case for the motions at right angles only. The detailed analysis of the strict averaging is, however, too lengthy for inclusion in this text, and reference should be made to the noteworthy deduction as given in the appendix of O. E Meyers' "Kinetic Theory of Gases."[2] It is of interest to observe that if $\bar{c}_1 = \bar{c}_2$ this term gives the Maxwell free path.

One more case of interest now demands attention and that is the question of the free path of a σ_1 molecule in a gaseous mixture of N_1 molecules of the σ_1 type and N_2 molecules of the σ_2 type per cm³. To get this, one can reflect that $\bar{c}_1$, the average velocity of the σ_1 molecule, divided by L_{12}, the mean free path of that molecule in the mixture, gives the number of molecular encounters Γ_1 per second of a σ_1 molecule with σ_1 and σ_2 molecules. If there are N_1 of the molecules in a cm³, the σ_1 molecule will collide with

$$\frac{\bar{c}_1}{L_1} = \pi\bar{c}_1\sqrt{2}\,\sigma_1^2 N_1$$

of molecules of its own kind per second. If there are N_2 of the σ_2 molecules in a cm³ the σ_1 molecule will collide with $\frac{\bar{c}_1}{L_2} = \bar{c}_1\pi\sigma_{12}^2 N_2 \sqrt{\bar{c}_1^2 + \bar{c}_2^2}/\bar{c}_1$ of the σ_2 molecules per second. Thus the number of impacts per second of the σ_1 molecule will be

$$\Gamma_1 = \sqrt{2}\pi N_1\bar{c}_1\sigma_1^2 + \pi\sigma_{12}^2 N_2\sqrt{\bar{c}_1^2 + \bar{c}_2^2}.$$

Since $L_{12} = \frac{\bar{c}_1}{\Gamma_1}$, then

$$L_{12} = \frac{1}{\sqrt{2}\pi N_1\sigma_1^2 + \pi N_2\sigma_{12}^2\sqrt{\bar{c}_1^2 + \bar{c}_2^2}/\bar{c}_1}.$$

Similarly, the mean free path L_{21} of the σ_2 molecules in the mixture will be

$$L_{21} = \frac{1}{\sqrt{2}\pi N_2\sigma_2^2 + \pi N_1\sigma_{12}^2\sqrt{\bar{c}_1^2 + \bar{c}_2^2}/\bar{c}_2}.$$

39. Mean Collision Frequency of Molecules of a Given Speed, Mean Free Path of Such Molecules, Tait's Free Path. In Sec. 37 the Maxwell free path for molecules moving with a Maxwellian distribution of velocities was deduced. This deduction gave the mean free path by dividing the average speed $\bar{c}$ by the mean numbers of collisions per second averaged over all molecules. The deduction was made by computing the average value of the collision frequency for molecules moving with a Maxwellian distribution, and dividing this into $\bar{c}$. The process by which this was accomplished can be seen in Secs. 18 and 37, where it is deduced. The matter may be regarded in another light, however, which leads to different results. It is obvious that the collision frequency Z must depend on the velocity of the molecule considered. If one can calculate Z, this frequency for a molecule of speed c, then one can calculate the mean free path of a molecule of speed c among the other molecules moving with Maxwell's

distribution of velocities. This will lead to a value for the mean free path L_c of a molecule of velocity c. It is of importance to know this quantity for such a molecule, and it will, accordingly, be calculated in what follows. Having this, it is then possible to determine the average value of L for L_c averaged over all possible speeds. Such an average path, designated by L_T, is numerically different from the ratio of the averaged velocity and collision frequency of Maxwell. As both are used in calculations, it is essential to know both values. Different modes of averaging are appropriate to the different problems of kinetic theory in which the mean free path plays a part, just as variously averaged speeds are useful in discussions involving the molecular speeds. It may be pointed out that the Maxwell free path is the one commonly used by physicists in developing approximate discussions along kinetic-theory lines. The legitimacy depends on the particular use of the free path, and it is questionable whether either is more universally serviceable.

If the attention be fixed on those molecules which have a particular speed, it is evident that the mean number of collisions per second of such molecules with all others will depend on the speed of the molecules under consideration. The evaluation *of this mean number of collisions per second, Z,* for molecules of speed c moving in a gas in which the most probable molecular speed is α, will now be carried out.

On the average, a molecule of speed c will collide in unit time with all of the molecules of speed c' contained in a cylinder whose base is $\pi\sigma^2$ and whose height is the relative velocity

$$V_r = \sqrt{c^2 + c'^2 - 2cc' \cos \theta},$$

θ being the angle between c and c'. Choose polar coordinates having the direction of c as axis, then θ and ϕ give the direction of the velocity of the other molecule c'.

By Sec. 34 the number of molecules in unit volume for which c' lies between c' and $c' + dc'$, θ between θ and $\theta + d\theta$, and ϕ between ϕ and $\phi + d\phi$ is

$$\frac{N}{\pi^{3/2}\alpha^3} c'^2 e^{-\frac{c'^2}{\alpha^2}} dc' \sin \theta d\theta d\phi,$$

so that the mean number of collisions per second will be

$$\frac{N\sigma^2}{\alpha^3\sqrt{\pi}} V_r c'^2 e^{-\frac{c'^2}{\alpha^2}} dc' \sin \theta d\theta d\phi.$$

The total number of collisions per second experienced by a molecule of speed c is obtained by integrating this with respect to c' from 0 to ∞, to θ from 0 to π, and to ϕ from 0 to 2π. Integration with respect to ϕ is effected at once by merely writing in 2π for $d\phi$. Integration with respect to θ may be conveniently carried out by using the relative velocity as variable. One has

$$V_r dV_r = cc' \sin\theta d\theta.$$

Making these substitutions, the total number of collisions per second experienced by a molecule of speed c may be expressed by

$$2\sqrt{\pi}\,\frac{N\sigma^2}{\alpha^3}\,\frac{c'}{c}\,V_r^2 e^{-\frac{c'^2}{\alpha^2}}\,dc'dV_r.$$

The integration limits with respect to V_r are as follows:

	$c' < c$	$c' > c$
$\theta = 0$	$V_r = c - c'$	$V_r = c' - c$
$\theta = \pi$	$V_r = c + c'$	$V_r = c' + c$

so that integration with respect to V_r yields two different expressions according to the relative sizes of c' and c. These are

$$\int V_r^2 dV_r = \frac{1}{3}[V_r^3] = \begin{cases} \frac{2}{3}c'(c'^2 + 3c^2) & c' < c \\ \frac{2}{3}c(c^2 + 3c'^2) & c' > c \end{cases}.$$

The total number of collisions is now to be obtained by integrating over all values of c' from 0 to ∞, using the appropriate integral according as $c' < c$ or $c' > c$, *i.e.*,

$$Z = \frac{\sqrt{\pi}N\sigma^2\alpha^2}{c}\left[\frac{4}{3}\int_0^c \frac{c'^2}{\alpha^5}(c'^2 + 3c^2)e^{-\frac{c'^2}{\alpha^2}}dc' + \frac{4}{3}\frac{c}{\alpha^5}\int_c^\infty c'(c^2 + 3c'^2)e^{-\frac{c'^2}{\alpha^2}}dc'\right].$$

It will be observed that the terms in the brackets are physically dimensionless. They form a function of a variable $x = \frac{c}{\alpha}$ defined by means of integration with respect to the variable $y = \frac{c'}{\alpha}$. The factor outside the brackets has the dimensions of reciprocal time as it should have.

The mean number of collisions per second is thus:

$$Z = \sqrt{\pi}N\sigma^2\alpha \cdot \frac{\Psi(x)}{x},$$

in which $\Psi(x)$ stands for the terms in brackets, *i.e.*,

$$\Psi(x) = \frac{4}{3}\int_0^x (y^4 + 3x^2y^2)e^{-y^2}dy + \frac{4}{3}\int_x^\infty (x^3y + 3xy^3)e^{-y^2}dy, \text{ and}$$

$x = \dfrac{c}{\alpha}$.

This function can be reduced to somewhat simpler terms by means of the integration formula

$$\int x^n e^{-x^2}dx = \frac{n-1}{2}\int x^{n-2}e^{-x^2}dx - \frac{1}{2}x^{n-1}e^{-x^2},$$

the result being

$$\Psi(x) = xe^{-x^2} + (2x^2 + 1)\int_0^x e^{-y^2}dy.$$

From this formula values of $\Psi(x)$ and related functions have been computed and may be found in tables.[3]

The result of the analysis is this: The mean number of collisions per second experienced by a molecule of speed $c = x\alpha$, where α is the most probable speed, is given by

$$Z = \sqrt{\pi}N\sigma^2\alpha\frac{\Psi(x)}{x},$$

where the factor $\dfrac{\Psi(x)}{x}$ can be obtained from the tables.

Thus the mean collision frequency of molecules of a given speed has been found to depend on the particular speed of the molecules considered. Their mean free path, similarly, depends on the speed, since

$$L_c = \frac{c}{Z},$$

in which c is the speed and Z the mean collision frequency of the molecules chosen.

Applying the expression for Z from above the result is, for L_c, the mean free path of the molecules of speed c in a gas in which the most probable speed is α

$$L_c = \frac{x^2}{\sqrt{\pi}N\sigma^2\Psi(x)}$$

wherein $x = \dfrac{c}{\alpha}$.

This formula might be written:

$$L_c = \frac{1}{\pi N\sigma^2}\cdot\frac{\sqrt{\pi}x^2}{\Psi(x)},$$

in which form it is recognized that the first factor is the Clausius free-path formula for the case where all the molecules are at

rest save the one whose free path is under consideration (Sec. 16). This corresponds to the free path in the present analysis of a molecule for which x is very large. The second factor may thus be regarded as a correction factor which allows for the fact that the molecule under consideration does not move with infinite speed with respect to the others. Values for the second factor may be found in tables.[3]

Starting with the assumption of a free path varying with the speed as deduced above, Tait calculated a new mean free path. Tait's calculation of the mean free path differs from that of Maxwell in that it starts from the formula for the mean free path of molecules of a given speed c and averages the values of L_c, weighting them according to the distribution of velocities. Tait's free path is thus given by:

$$L_T = \frac{1}{\pi N\sigma^2}\int_0^\infty \frac{4x^4 e^{-x^2}dx}{\psi(x)}.$$

The definite integral occurring here has been computed by Tait, who finds the value 0.677, so that the Tait free path is

$$L_T = \frac{0.677}{\pi N\sigma^2}.$$

It is important to see why Tait's free path differs from that of Maxwell. Examination of the derivations of the two that have been given will show that Maxwell's free path is obtained by dividing $\bar{c}$, the mean speed, by Z, the mean number of collisions per second averaged over all the molecules. On the other hand, Tait takes the value of the free path $\frac{c}{Z}$ appropriate to each speed and averages this over all the molecules. Obviously, still another free path would be obtained if the mean value of the speed $\bar{c}$ were to be multiplied by the value of $\frac{1}{Z}$ averaged over all the molecules, and still others could be obtained by averaging in different ways. These will all depend on $\frac{1}{N\sigma^2}$ for their order of magnitude, but will differ in the value of the numerical factor for much the same reason that the root-mean-square speed of the molecules is not the same as the arithmetic mean of the speeds.

40. Number of Molecules Striking Unit Surface per Second.[4] — An excellent illustration of the application of the distribution law

is given by the rigorous calculation of the number of molecules striking unit surface per second. Take an element of surface ds, and consider an element of volume dv with N molecules per cc in it. Then in dv there are Ndv molecules. This volume is r cm from ds along a line making an angle θ with the normal to ds (Fig. 21). The volume dv may then be written $dv = dr \times rd\theta \times r \sin \theta d\phi$. Of these $Nr^2 \sin \theta d\theta d\phi dr$ molecules, the number which have a velocity between c and $c + dc$, are, by Maxwell's law,

$$\frac{4}{\alpha^3\sqrt{\pi}} c^2 e^{-\frac{c^2}{\alpha^2}} dcNr^2 \sin \theta d\theta d\phi dr.$$

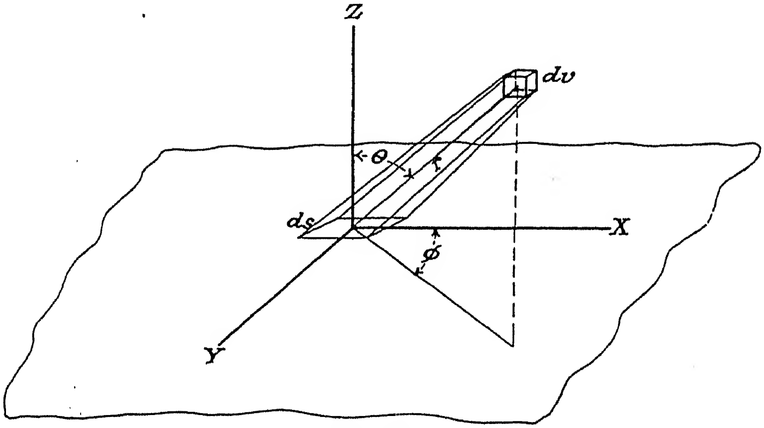

FIG. 21.

Now each of these starts *a new path* $B = \frac{\bar{c}}{L}$ times a second, where $\bar{c}$ is the *average speed*, and L is the mean free path. The number that leave dv per second moving towards ds with a velocity between c and $c + dc$ is B times the number of molecules above. Of these only the molecules emitted in the solid angle subtended at dv by ds will reach ds. This fraction is given by the ratio of the area $ds \cos \theta$ to the total surface of the sphere $4\pi r^2$ which molecules from dv going r penetrate. The number of molecules that leave dv and that are headed for ds is given by

$$\frac{4NB}{\alpha^3\sqrt{\pi}} e^{-\frac{c^2}{\alpha^2}} dcr^2 \sin \theta d\theta d\phi dr \frac{ds \cos \theta}{4\pi r^2}.$$

But of those headed for ds only those cross it that go a distance r or more without an impact. The fraction going r or more with-

out an impact is given from the law for the distribution of free paths as $e^{-\beta r}$, where

$$\beta = \frac{1}{L} = \frac{B}{c}.$$

Hence the number of molecules leaving dr per second that strike ds is given by

$$N_{dvds d\theta} = \frac{4NB}{\alpha^3\sqrt{\pi}} e^{-\frac{c^2}{\alpha^2}} c^2 dc r^2 \sin\theta d\theta d\phi dr \frac{ds\cos\theta}{4\pi r^2} e^{-\beta r}.$$

The number which strike ds per second from the whole space above is obtained by integrating r from 0 to ∞, θ from 0 to $\frac{\pi}{2}$, ϕ from 0 to 2π, and c from 0 to ∞. Hence the number of molecules striking ds per second from above is

$$N_{ds} = \frac{N}{\alpha^3\pi^{3/2}}\int_0^\infty c^3 e^{-\frac{c^2}{\alpha^2}}dc \times B\int_0^\infty e^{-\beta r}dr\int_0^{\frac{\pi}{2}}\sin\theta\cos\theta d\theta\int_0^{2\pi}d\phi ds$$
$$= \frac{N}{\alpha^3\pi^{3/2}}\left(\frac{\alpha^3\pi^{1/2}}{4}\right)B\left|-\frac{1}{\beta}e^{-\beta r}\right|_0^\infty \times \frac{1}{2} \times 2\pi ds.$$

Since $\beta = \dfrac{B}{\bar{c}}$,

$N_{ds} = \dfrac{N\bar{c}}{4}ds$, where $\bar{c}$ is the average speed. $\dfrac{N_{ds}}{ds} = \nu$ is the number striking 1 cm² per second, so that

$$\nu = \frac{N\bar{c}}{4} = \frac{NC\sqrt{8/3\pi}}{4} = \frac{NC}{\sqrt{6\pi}}.$$

An interesting application of this law may be made to aid in calculating the vapor pressure of a substance. This has actually been done by Langmuir.[4] Quoting from a paper by Langmuir:

> Let us consider a surface of metal in equilibrium with its saturated vapor. According to the kinetic theory, we look upon the equilibrium as a balance between the rate of evaporation and rate of condensation. That is, we conceive of the time processes as going on simultaneously at equal rates.
>
> At temperatures so low that the vapor pressure of a substance does not exceed a millimeter, we may consider that the actual rate of evaporation of a substance is independent of the presence of vapor around it.

This merely means that the presence of atoms or molecules of the vaporizing substance at a mm pressure does not interfere with evaporation by acting as a reflecting layer that throws the evap-

orating molecules back to the surface on their first free path. This action is not taken into account in deducing the equation above, "that is, the *rate of evaporation* in a high vacuum is the same as the rate of evaporation in the presence of the saturated vapor" under these conditions. "Similarly, we may consider that the rate of condensation is determined only by the pressure of the saturated vapor." To see how this works the equation may be transformed as follows. Multiply $\nu = \frac{N\bar{c}}{4}$ by m, the mass of a molecule, then $m\nu$ is the weight w of substance striking a cm² of surface per second and thus also evaporating. Thus

$$w = m\nu = \frac{Nm\bar{c}}{4} = \frac{\rho\bar{c}}{4},$$

where Nm is the density ρ. But $\rho = \frac{M}{V} = \frac{Mp}{pV} = \frac{Mp}{RT}$, where p is the pressure, and M is the mass of vapor in volume V of a mol. Also $C = \sqrt{\frac{3p}{\rho}}$, and as $\bar{c} = \sqrt{\frac{8}{3\pi}}\,C$, $\bar{c} = \sqrt{\frac{8p}{\pi\rho}} = \sqrt{\frac{8p}{\pi Mp/RT}} = \sqrt{\frac{8RT}{\pi M}}$. Therefore

$$w = \frac{1}{4}\frac{Mp}{RT}\sqrt{\frac{8RT}{\pi M}} = p\sqrt{\frac{M}{2\pi RT}}$$
$$= 43.74 \times 10^{-6}\, p\sqrt{\frac{M}{T}}.$$

Here M is the molecular weight, T is the absolute temperature, p is in dynes per cm², and w is the weight evaporated per cm² per second. For tungsten at 2800°abs., Langmuir found w, the loss in weight, to be 0.43×10^{-6} grams, per cm² per second. This gives $p = 28.6 \times 10^{-6}$ mm of Hg as the vapor pressure of W at this temperature.

41. Experimental Verification of the Maxwellian Distribution of Velocities.—Up to the present no direct and precise verification of the distribution law has been achieved. Three experimental tests have been made. The first of these is direct but inexact, although capable of much greater precision than was obtained. The other two are indirect and depend on assumptions more or less justified. They lead to results that are, however, more precise. The first method is due to Stern.[5] It consists in measuring the displacement of the deposit of silver from a stream of silver atoms moving with their thermal velocities, due to the

rapid movement at right angles to the stream, of the plate on which they are deposited. The second method is due to O. W. Richardson.[6] The latter directly measured the velocity distribution of electrons emitted from an incandescent source. The assumption made is that the electrons are emitted as a result of their heat motions and are in thermal equilibrium with the atoms of the metal when they leave, thus possessing a Maxwellian velocity distribution. The last method depends on the Doppler effect,[8] due to the thermal velocities, on atoms emitting spectral lines in a discharge tube. It was suggested by Lord Rayleigh,[10] and carried out first by Michelson[9] and later by Fabry and Buisson.[11] As the Doppler shift is too small to be observed directly, it is obtained by an analysis of the width of the lines by a measurement of the path difference over which interference fringes are visible. All three methods agree with the predictions from the distribution law within the limits of accuracy of the experiments.

42. The Average Velocities of Molecules or Electrons Emitted from Hot Bodies.—If an enclosure containing atoms, molecules, or electrons in equilibrium at a temperature T is considered the distribution of velocities is at once defined by the evaluation of α (the most probable speed) from the temperature. Thus in Sec. 5 it was found that $pv = RT = \frac{1}{3}\nu m\bar{c}^2$. Hence, dividing by ν, the number of molecules present in the volume v, one can write $m\bar{c}^2 = 3\frac{R}{\nu}T$. Calling $\frac{R}{\nu} = k$, one obtains $\frac{1}{2}m\bar{c}^2 = \frac{3}{2}kT$.*

From the above, $C = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$, where m is the weight of a molecule and M is the weight of a gram-molecule, R being given for a gram-molecule. Since $\alpha\sqrt{3/2} = C$ or $\alpha = \sqrt{\frac{2kT}{m}}$, it is seen at once that the number of molecules having a velocity c in the enclosure is expressed by the equation

$$N_{dc} = \frac{4N}{\alpha^3\sqrt{\pi}} c^2 e^{-\frac{mc^2}{2kT}} dc. \quad \text{(See Sec. 36.)}$$

If a small opening be made in the enclosure so that the molecules can stream out into an evacuated space, the average velocity of the molecules emitted will not be the same as the average

* The quantity k is known as the Boltzmann constant and it is the value of the gas constant k per molecule in equilibrium. R is the gas constant for the number of molecules ν. The $\bar{c}^2$ here is really the C^2 of Sec. 35.

velocity of the molecules existing in the enclosure, as a little consideration will show. The molecules inside were in equilibrium. Those issuing are not, and the number issuing in unit time is the greater the greater the velocity of thermal agitation of the molecules, for it is only by virtue of their velocities that they can emerge. Hence the chance of a molecule emerging is proportional to its velocity. The number emerging at a given velocity c will then depend on the product of the number N_{dc} of particles of that velocity present and the value c of the velocity. Thus the average velocity in such a steam C_1 will not be that given by $C = \sqrt{\frac{3kT}{m}}$, but will be greater than this. It may be found as follows: In getting C^2 in Sec. 35 its value was obtained by multiplying N_{dc} by c^2, integrating it from zero to infinity, and dividing it by the integral of N_{dc} from zero to infinity, which was N. To find the value of C_1^2 under the conditions of the emitted beam, the product of c^2 into the number of molecules N'_{dc} in the stream which have a velocity c, to wit cN_{dc}, must be integrated from zero to infinity and divided by the integral of the number of particles issuing with a velocity c (*i.e.*, cN_{dc}), taken from zero to infinity; that is, the value of C_1^2, the average in a stream, is given by

$$C_1^2 = \frac{\int_0^\infty \frac{4N}{\alpha^3\sqrt{\pi}} c^2 \times c \times c^2 e^{-\frac{c^2}{\alpha^2}} dc}{\int_0^\infty \frac{4N}{\alpha^3\sqrt{\pi}} c \times c^2 e^{-\frac{c^2}{\alpha^2}} dc} = 2\alpha.$$

In the inside of the oven $C^2 = \frac{3}{2}\alpha$, hence $C_1^2 = \frac{4}{3}C^2$, $C_1 = \sqrt{\frac{4C^2}{3}} = \sqrt{\frac{4kT}{m}}$. Thus the average velocity of the molecules in such a stream is $C_1 = \sqrt{\frac{4kT}{m}}$ in contrast to the average value $C = \sqrt{\frac{3kT}{m}}$ inside the oven.

43. The Rate of Escape of Molecules from a Hot Surface, and the Distribution of Velocities after Escape.—In one of the proofs of the distribution law it will be essential to know the number of molecules or electrons escaping from a heated surface having a component of velocity u normal to the surface. From the evaluation of this quantity it is also possible to show that the dis-

tribution of velocity among the escaping molecules is independent of the work done in passing through the surface, a fact which simplifies the considerations involved. Thus it seems of interest to investigate these points in what follows. In this discussion the molecules below a bounding surface may be assumed in equilibrium with a source of energy. A certain number of these are passing outward each instant in virtue of their heat motions. The number of such that leave may be found as follows: It is obvious that the component of velocity u normal to the surface is the only one effective in driving them through it. If there *are N molecules per cm³* present, the number with a velocity component u which would strike an area ds in a time dt are those lying in a cylinder of length udt and base ds. That number is $Nudtds$. Of these N molecules per cm³, only $f(u)du$ have a velocity between u and $u + du$. Hence, if ds is 1 cm and dt is 1 sec, the number passing through 1 cm² per second is

$$N_{(u)}du = \frac{Nu}{\alpha\sqrt{\pi}}e^{-\frac{u^2}{\alpha^2}}du.$$

For the type of applications to be made it is simpler to transform this equation by introduction of a new set of constants. Since these constants are frequently encountered in published papers, their introduction will not be amiss at this point. It was found that in equilibrium $C^2 = \frac{3kT}{m}$. If one calls $h = \frac{1}{2kT}$, then $C^2 = \frac{3}{2mh}$. Since $C^2 = \frac{3}{2}\alpha^2$, therefore $\alpha = \sqrt{\frac{1}{mh}}$. The above equation then becomes

$$N_{(u)}du = N\left(\frac{hm}{\pi}\right)^{\frac{1}{2}}ue^{-hmu^2}du.$$

The number of molecules having all sorts of velocity components u normal to the surface that pass out through 1 cm² per second is obtained by integrating $N_{(u)}du$ from 0 to infinity. That is

$$\eta = \int_0^\infty N_{(u)}du = \frac{N}{2(\pi hm)^{\frac{1}{2}}}.$$

From this $N = 2\eta(\pi hm)^{\frac{1}{2}}$ and so

$$N_{(u)}du = 2hmu\eta e^{-hmu^2}du.$$

Hence the probability that a molecule will leave a surface in a gas with a velocity component perpendicular to it lying between u and $u + du$ is given by $N_{(u)}du/\eta$, or

$$F_{(u)}du = 2hmue^{-hmu^2}du.$$

If now the hypothetical surface through which the molecules above escaped be replaced by a physical boundary, in escaping through which the molecules have to do work, the question presents itself whether the escaping molecules will maintain the same velocity distribution after escaping as they had before. Assume that u_1 be the velocity of the molecule impinging on the surface, and u_0 be the velocity on leaving the surface. Then it can be shown that $u_0^2 = u_1^2 - \frac{2}{m}\phi$, where ϕ is the change in the work function in passing through the surface. The number of particles *escaping per second* with velocity between u_0 and $u_0 + du_0$ will be the same as the number of molecules *impinging on the inside* of the surface for which the normal velocity component to the surface lies between u_1 and $u_1 + du_1$. Since $u_0^2 = u_1^2 - \frac{2\phi}{m}$, one may write $u_0 du_0 = u_1 du_1$, whence, as $\eta_0(u_0)du_0 = \eta_1(u_1)du_1 = N\left(\frac{hm}{\pi}\right)^{1/2} u_1 du_1 e^{-hmu_1^2}$,

$$\eta_0(u_0)du_0 = N\left(\frac{hm}{\pi}\right)^{1/2} u_0 du_0 e^{-hm\left(u_0^2+\frac{2}{m}\phi\right)}.$$

Here N is the number of molecules per cm³ inside the boundary. Those molecules which escape per second have $u_0 > 0$, so that it is possible to write that the number that escape per second η_0 are given by

$$\eta_0 = N\left(\frac{hm}{\pi}\right)^{1/2} \int_0^\infty u_0 e^{-hm\left(u_0^2+\frac{2}{m}\phi\right)} du_0$$

$$= \frac{N}{2} \frac{e^{-2h\phi}}{(\pi hm)^{1/2}}.$$

Therefore N is given by $\frac{2\eta_0(\pi hm)^{1/2}}{e^{-2h\phi}}$

Thus,

$$\eta_0(u_0)\, du_0 = 2hu_0\eta_0 e^{-hmu_0^2} du_0$$

Whence $F(u_0)du_0$, the probability that a molecule of the emerging group have a velocity between u_0 and $u_0 + du_0$, is obtained from

$$F(u_0)du_0 = \frac{\eta_0(u_0)du_0}{\eta_0} = 2hmu_0 e^{-hmu_0^2} du_0.$$

This is exactly the same form as the probability that the molecules of velocity u_1 will impinge on the inside of the surface which was $F(u)_1 du_1 = 2hmu_1 e^{-hmu_1^2} du_1$ and which was a direct

consequence of the Maxwell's distribution of velocities inside the boundary. Thus one can conclude that the distribution law is unchanged when the molecules do work in going through the surface. It can be shown that the distribution parallel to the surface will also be unaltered. Thus the distribution of velocities among the molecules or electrons leaving a surface is completely independent of the work done in going through the surface (see also Sec. 84).

44. Measurement of Molecular Velocities by the Rotating-plate Method. Stern[3] made a direct measurement of the velocity $C_1 = \sqrt{\frac{4RT}{M}}$ with which atoms of silver leave a surface of molten silver at a temperature T in a vacuum. From an incandescent wire W in Fig. 22 coated with silver a stream of silver atoms is projected in all directions. By means of a slit in the diaphragm D the part of the stream escaping towards the plate P is confined to a narrow wedge-shaped prism which produces, when condensing on the plate P, a sharply defined narrow band A. If, now, the slit

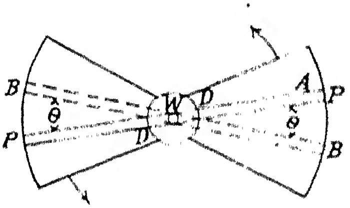

FIG. 22.

and the plate are set in rapid rotation about the wire W, then, while the atoms travel from W to P, the plate rotates through a finite angle, the band produced by the condensed silver atoms will be deflected to a point away from the position of the band produced when at rest in a direction opposite to that of the rotation by an amount depending on the velocity of rotation, say to B. For simplicity, assume that D is very close to W. Then calling the distance DP, L, the time taken for the atom of velocity $c = \sqrt{C_1}$ to fly from D to P is $\tau = \frac{L}{c}$. If the plate rotates ν times a second, the plate moves $2\pi L\nu\tau$ cm in the time τ. Thus a single atom of velocity c will have its point of incidence on the resting plate displaced a distance s when the plate rotates, given by the relation $s = 2\pi L\nu\tau = 2\pi\frac{L^2\nu}{c}$. Thus, if the beam were infinitely thin, since other atoms have all velocities given by Maxwell's law, it would be spread out into a diffuse displaced band whose maximum corresponded to an α which is $\sqrt{2/3}\,C_1$. If

this maximum could be located, then the value of s could be measured by its displacement from the undisturbed line, and hence, knowing L and ν, v could be at once computed. If the value of v so obtained was found to be equal to that obtained by an optical measurement of the temperature of the filament as given by $C_1 = \sqrt{\frac{4RT}{M}}$ then the distribution law would be partially proved as regards the actual values of the velocity. A more complete proof would come from an actual study of the distribution of the silver atoms deposited on the plate in the displaced deposit.

In practice, certain approximations had to be made to simplify the experiment. The distance L was not a constant in practice, owing to the length of the filament. Calling a the distance from P to W, and b the half length of the filament at W, then L lies between a and $\sqrt{a^2 + b^2}$. Its average distance is $a\left(1 + \frac{1}{2}\frac{b^2}{a^2}\right)$. For the experiments performed, a was 6 cm and b was 1.5 cm. The error in taking $L = a$ was about 3 per cent. Furthermore, since the length WD is finite compared to DP, a correction must be made for this. Calling DP, L_1 and WD, L_2, the correct equation for small values of s, the displacement, is $s = \frac{2\pi\nu L_1 L_2}{v}$.

The system of wire slit and plate, which for mechanical balance had two slits and two plates mounted on the same straight line as the filament W, were placed in a frame which could be rotated by means of the shaft from a motor which was coaxial with the length of the filament. The shaft passed from the gas-tight glass housing carrying this part of the apparatus through a complicated series of packing glands to the motor. The housing was pumped out to 0.0001 mm and the speed of the motor used was 1500 r.p.m. in the first experiments and 2700 r.p.m. in later ones.

In actual experiments the direction of rotation of the motor was reversed, so that the distance between the maxima of the two displaced lines could be measured. The double deflections so produced were between 0.7 and 0.8 mm at 1500 r.p.m. and between 1.26 and 1.12 mm. at 2700 and 2400 r.p.m.

Another correction has to be made in the computation. The distance from the maximum of one line to that of the other when halved gives $\alpha = C_1\sqrt{2/3}$, provided the beam had a negligible width to begin with. But for practical purposes this was impossi-

ble. Analysis will show that j_a, the intensity of the deflected beam at s cm. from the undeflected beam, is given by the relation

$$j_a = j_0 \frac{4}{\sqrt{\pi}} \int_{\frac{S_\alpha}{S + d/2}}^{\frac{S_\alpha}{S - d/2}} x^3 e^{-x^2} dx$$

for the case of atoms with the distribution resulting from the emission from the filament. Here S_α is the deflection for the most probable speed that is sought, and would be given by the maximum for a spot which was infinitely thin, with the plates at rest. The integration shows that the maximum observed for an undeflected spot of width d would be *closer to the undeflected spot* than the true value of α. Hence, knowing d, and measuring the distance between the maxima produced by changing the direction of rotation, the true deflection for the most probable speed S_α can be measured. Evaluation for the correction for this width of the slit in the experiments with 1500 r.p.m. yielded 0.1 mm. Hence the deflection S corresponding to the true value of c and used in its evaluation was 0.45 to 0.50 mm in place of the values 0.35 to 0.40 mm observed. The early values obtained by Stern at 1500 r.p.m. were compared with the velocities of atoms computed from the estimated value of the filament temperature and found to agree. As there were errors in this calculation, due to Stern's neglect of the higher average velocity of the emitted atoms, these results will not be given. The deflections S_α observed at 2700 and 2400 r.p.m., of 1.20 and 1.12 mm., yielded corrected values of 675 and 643 meters per second for C_1. The value for C_1 computed for 1200°C. was 672 meters per second, in accord with the values observed within the limits of experimental error.

These experiments are capable of a far greater precision than was obtained. It would seem worth while to have them extended in driving plates by means of a high-speed air turbine or motor acting on the moving system in its glass casing by means of a magnetic coupling. An electrically heated oven whose temperature could be measured optically could also be used. The present experiments were not carried further by Stern because they showed, from the value of the velocities obtained, that the silver evaporated in the *atomic* form. This discovery and the application of the technique developed in the preliminary experiments reported above led Stern at once to his now classical experiments

proving the spatial magnetic quantization of the silver atoms in divergent magnetic fields.

45. Distribution of Velocities among Electrons Liberated from an Incandescent Source.—A theoretical study of the behavior of electron atmospheres[13] has shown that these are in all respects analogous to gaseous atmospheres. They differ from them chiefly in the smaller masses of the electrons and their mutual repulsion due to their charges. For the great attenuation of the atmospheres in a number of experiments the distances between individual electrons becomes so great that the potential energy of the forces of repulsion are negligible compared with the kinetic energies possessed by the electrons at those temperatures. Thus the electrons sensibly obey the laws of a perfect gas, *i.e.*, $pv = RT$, or $p = NkT$, where N is the number of electrons per cm^3, k is the gas constant per electron or per molecule, and T the absolute temperature. Hence it would not be surprising to find that in such an atmosphere the average kinetic energy of one electron is $\frac{3}{2}kT$ and that the energies are distributed according to the Maxwell distribution law.

Now it was at one time believed that these electron atmospheres existed even in the interiors of metals, and that thus the electrons might be in thermal equilibrium with the atoms of the metal.[14] Thus on heating a metal, if the Maxwell distribution law held inside the metal, electrons emitted because of their heat motions would, by Sec. 43, be expected to show this same distribution outside. This assumption, according to Richardson,[6] may be applicable even if the electrons are emitted from the surface and flow away constantly without attaining a steady state. Whether the Maxwellian distribution exist in the dense electron atmospheres assumed inside the metal surfaces, or even whether such atmospheres exist at all (a point which is at present open to a reasonable doubt), the fact remains that Richardson has predicted that the electron streams emitted from the surfaces of incandescent metals have the energies corresponding to electrons in thermal equilibrium with the surface, and that their energies are distributed according to Maxwell's distribution law. Such a definite prediction deserves experimental test. If it is found to correspond to fact, then it is a fact of great importance whether the initial assumptions of Richardson (which he has in part modified) are correct or not, for no matter what the mecha-

nism is, one would have definite proof that electrons emitted by a hot body are: (1) in temperature equilibrium with it according to the law of equipartition and of Maxwell, and (2) that the electrons have a distribution of velocities predicted by Maxwell's law. Thus one would have a directly measurable quantitative verification of a Maxwellian distribution of velocities existing in the heat motions of particles of matter. This point must be stressed, for except for the two other proofs which are given in this chapter, both of which depend on the constants deducible from the Maxwell law, no direct verification of the distribution exists. Outside of these three experimental verifications, the distribution law is unproved experimentally, for it only appears in constants of the kinetic theory whose value is the subject of dispute owing to uncertainties in averaging. Thus the experimental verification of such constants up to the present furnishes no certain proof of the validity of the present law, and all available evidence is of value.

In Secs. 42 and 43 the average velocity C_1 of particles escaping from the surface of a hot source and the number of emitted particles having a component of velocity between u and $u + du$ normal to the surface were deduced. The number of electrons emitted with velocity components between u and $u + du$ along x, the normal to the surface of a platinum ribbon lying in the y, z plane per second, was

$$N_{(u)}du = \eta 2hmue^{-hmu^2}du.$$

In this equation η was the total number of electrons emitted from the surface in unit time. For the components parallel to the surface of the ribbon, to wit y and z, it is possible to write at once

$$N_{(v)}dv = \eta\sqrt{\frac{hm}{\pi}}e^{-hmv^2}dv,$$

$$N_{(w)}dw = \eta\sqrt{\frac{hm}{\pi}}e^{-hmw^2}dw,$$

for the y and z components have the same values inside a surface or plane as when emitted outside, the number of electrons with these components emitted being uninfluenced by their velocities.

If the yz plane of the ribbon form part of one plate L of a parallel plate condenser, the other plate of which is U, the electrons going from L to U in virtue of their thermal velocities in a complete vacuum will constitute a current from U to L. This current can be measured by an electrometer attached to U. If

the plates are close enough together so that the radius of the plates is great compared to the distance between the plates, few electrons will escape laterally from between the plates. Also the lines of force between the plates will be uniformly distributed, parallel, and sensibly in the direction of the x-axis. Let a potential V be applied between the plates. The equations of motion of an electron at any point between them will be

$$m\frac{\partial^2 x}{\partial t^2} = m\frac{\partial u}{\partial t} = -\epsilon\frac{\partial V}{\partial x}$$

$$m\frac{\partial^2 y}{\partial t^2} = m\frac{\partial v}{\partial t} = 0 \text{ and } m\frac{\partial^2 z}{\partial t^2} = m\frac{\partial w}{\partial t} = 0.$$

Call $u = \frac{\partial x}{\partial t}$, whence, integrating the first expression,

$$u^2 = u_o{}^2 - \frac{2}{m}\epsilon V,$$

if u_o is the velocity of emission of the electron at $x = 0$ (*i.e.*, at L) and u is its velocity at a point where the potential is V. As ϵ is negative (for the charge of the electron is negative), if U be made negative V will be negative, and electrons will be repelled by the upper plate. Under these conditions u will become 0 at a point at which $V = \frac{mu_o{}^2}{2\epsilon}$. For this value of V the electrons of velocity u_o will leave L and be turned back at U returning to L. Electrons with a value of u_o greater than this will, however, still reach U. Thus by measuring the current to U for various values of V the current due to electrons which leave L with a velocity u_o equal to or greater than the one corresponding to the particular value of V chosen will be obtained. Thus by measuring $i = n\epsilon$, the current for a given V, the number of electrons n corresponding to those whose u_o is equal to or greater than the u_o given by $V = \frac{mu_o{}^2}{2\epsilon}$ is obtained. Thus if $F(u_o)du_o$ is the proportion of the electrons for which the u component lies between u_o and $u_o + du_o$, and if $f(v_o)dv_o$ and $f(w_o)dw_o$ represent the corresponding functions for the v and w components of velocity, the current to U will be given by

$$i = \eta\epsilon\int_{\sqrt{\frac{2\epsilon}{m}V_1}}^{\infty} F(u_o)du_o \int_{-\infty}^{+\infty} f(v_o)dv_o \int_{-\infty}^{+\infty} f(w_o)dw_o.$$

η is the number of electrons emitted per second by the source at all velocities. If Maxwell's law is correct, $F(u_o)du_o$ is none other than the quantity evaluated in Sec. 43, $2hmnu_o e^{-hmu_o^2}du_o$, and $f(v_o)dv_o$ and $f(w_o)dw_o$ are given at the beginning of this discussion. Integration yields

$$i = \eta\epsilon e^{-2hV_1\epsilon}$$

and since $\eta\epsilon$ is equal to i_o, the value of i, when V_1, the opposing field, is 0, then

$$\frac{i}{i_o} = e^{-2hV_1\epsilon}.$$

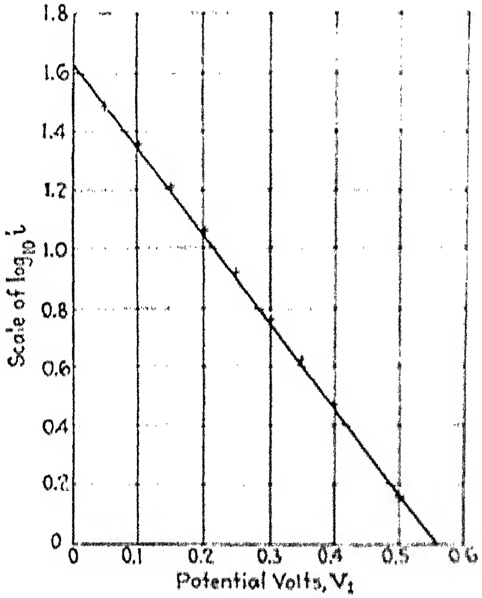

FIG. 23.

Now h was $\dfrac{1}{2kT}$ and taking the logarithms of both sides of the equation one obtains the simple relation:

$$\log\frac{i}{i_o} = -\frac{V_1\epsilon}{kT} = -\frac{N\epsilon}{RT}V_1, \text{ in which } \frac{1}{k} = \frac{N}{Nk} = \frac{N}{R},$$

N being the number of molecules per cm^3, and R the appropriate value of the gas constant for 1 cm^3 of gas. Now $N\epsilon$ is the Faraday constant of electrolysis divided by 22,400, and R is 3.711×10^3 ergs per degree Centigrade. Thus if Maxwell's distribution law has the same form as the distribution of electronic velocities,

$\log \frac{i}{i_o}$ plotted against V_1 should give a straight line. Now Richardson and Brown carried out this measurement of $\frac{i}{i_o}$ as a function of V_1 and the results of one set of measurements are shown in Fig. 23. It is seen at once that the relation between $\log \frac{i}{i_o}$ and V_1 is a linear one, and careful measurements have shown this to hold within the limits of experimental error, which is 1 per cent. Later measurements were made to verify the law for the components parallel to the emitting surface, and sufficiently close agreement was found to make this seem true if the results were taken in conjunction with the very nice verification in the case of the normal component.

Another equally important test to be obtained from these experiments was whether the average energy of the electrons was that to be expected from the distribution law and from the temperature of the filament, in other words, whether the electrons had the energy corresponding to the molecular energy of agitation at the emission temperature of the filament.

This can be tested easily as follows: If $\log \frac{i}{i_o}$ be measured as a function of V_1 the constant factor $\frac{N\epsilon}{RT}$ can be determined from the slope of the straight-line relation between $\log \frac{i}{i_o}$ and V_1. If the temperature T be determined optically from the filament, then, since $N\epsilon$ is known, R can be determined from the experiments and compared with the known value. In the early experiments, values of R between 4.36×10^3 and 3.08×10^3 were found as compared with 3.711×10^3, which is the true value. Two sources of error, however, existed, in the measurements, which were not eliminated in this work. Both were due to the heating current in the filament. This gave a fall of potential down the filament so that electrons had more than u_o for a velocity. Also the magnetic field produced by this current changed the paths of the electrons and thus disturbed the relation between u, v, and w. Schottky[15] ingeniously got around this difficulty by using an alternating-current device, heating the filament on one phase and cutting out the heating current in the next one while the measurements were being made. He obtained

values of R that were still too high but much closer than those of Richardson and Brown. In a recent paper Jones has eliminated a number of the errors inherent in Schottky's work and succeeded in obtaining value of R which deviated less than 15 per cent from the true value of R between temperatures of 1450 and 2000°K. The deviations were nearly equally great on both sides of the true value and the average deviation was about ± 5 per cent. Very recently the experiments of Jones were extended by Germer,[17] using a straight tungsten filament and a cylindrical electrode. He also used a device for heating his filament and measuring the thermionic currents when the heating current was off. Measurements were made at eight different temperatures from 1440 to 2475°K. Correcting for the contact difference of potential between the filament and the grid, it was found that at each temperature (except at very low voltages where the space charge effect limited the current) the *current varied with the voltage in just the manner calculated on the assumption that the electrons leave the filament with velocity components distributed according to Maxwell's law for an electron atmosphere in temperature equilibrium with the hot filament.* At 2475°K. the assumed *Maxwellian distribution was verified up to a retarding potential so great that only one electron in* 10^{10} *emitted electrons was able to reach the collector.* This accurate extension of the previous measurements verifies the law over a large range of temperatures, and over a remarkable range of velocities. It constitutes probably the best quantitative verification of the law, in that it verifies it over so great a range of velocities. Thus the fact must be accepted that no matter whether the theoretical assumptions are correct (1) the electrons are emitted from a hot metal with the mean energy which the Maxwell distribution law whould lead one to expect; and (2) the velocities are distributed among the electrons in accord with the Maxwellian law to within 1 per cent. Thus the Maxwellian law has been obtained and verified quite definitely in one case, *viz.*, that of the velocities of electrons which are purely of thermal origin.

46. The Verification of the Maxwell's Distribution of Velocities by the Doppler Effect in the Spectral Lines Emitted in a Discharge Tube.[7]*—Assume a group of particles all emitting light of a single wave length λ_0, or a frequency ν_0. If the par-

* The Author's acknowledgements are due to Methuen & Co. and to Dr. E. Bloch for permisson to use his own free translation of the section entitled "Largeuer de Raies Spectials" in Bloch's "Theorie Cinètique des Gaz."

ticles are at rest, then the light would be entirely monochromatic. Under these conditions the light from the source would be such that a portion of the train of waves would interfere with any other portion of the wave train, no matter how many waves intervened between the two portions of the train coming together under conditions where interference was possible. For example, in a Michelson interferometer, interference bands would be observed for light from such a source no matter whether one arm of the interferometer were 10 meters longer than the other one. If, now, one of two things occurred, this would cease to be possible. If the phase of the vibrations of the light centers in the atoms were disturbed through molecular impacts, then the interference over differences of path length corresponding to the number of waves emitted over a *free path only* could be observed. In the discharge-tube light sources used, however, such low pressures exist that this period is quite long. Thus the visibility of fringes is little altered by this cause. On the other hand, since the molecules or atoms are undergoing heat motions, the frequency of the light emitted by them undergoes a shift to longer or shorter wave lengths, depending on whether the atoms are moving away from or towards the observer. As all velocities exist on the distribution law, the initially monochromatic ray is broadened in both directions from ν_0 or λ_0, having a distribution of intensities in this finite band which is determined by Maxwell's law of distribution of velocities. This finite width of the spectral lines will act in such a fashion that after a path difference of many thousands of fringes the part of the fringes due to one portion of this band will be overlapped by the fringes produced by another portion of the band and the fringes will become indistinct. The rate of decrease in visibility of the fringes as a function of path difference must therefore depend on the width and distribution of intensities over the width of the band into which monochromatic lines are drawn out by the molecular velocities.

It now becomes necessary to study the change in visibility of fringes as a function of the breadth of spectral lines. If two monochromatic radiations of the same frequency ν and amplitude a meet with a phase difference θ, one can, in calling ϕ the phase of one of them, represent the resulting vibration by

$$a \cos \phi + a \cos (\phi + \theta) = 2a \cos \frac{\theta}{2} \cos \left(\phi + \frac{\theta}{2}\right).$$

The resulting intensity is given by

$$I = 4a^2 \cos^2 \frac{\theta}{2}.$$

Since the difference of phase θ for a path difference δ can be written as $2\pi \frac{\delta}{\lambda}$ (*i.e.*, 2π multiplied by the number of wave lengths in δ), and since $\lambda = \frac{V}{\nu}$, where V is the velocity of light and ν the frequency of the vibration, the above expression becomes

$$I = 4a^2 \cos^2 \frac{\pi \delta}{V} \nu.$$

Under conditions where there are, for a difference in path, whole multiples of half the wave lengths λ_0, the intensity is strictly 0 and the visibility of the fringes is independent of the path difference δ, for the cosine term only is a function of δ and varies from 0 to 1 with δ, while a is independent of δ, so that when the cosine is 1, I is always $4a^2$. Where the ray is not monochromatic, it must be divided into very narrow portions, each one corresponding to an interval $\Delta\nu$ for which the intensity of the fringes may be given by the above expression, but for which a^2 will depend on the intensity of the particular $\Delta\nu$ given. Thus if the intensity is found to vary with ν, the a^2 for each $\Delta\nu$ will then be a function of ν. The total intensity of the fringes observed would be $\int I d\nu$.

$$\int I d\nu = 4 \int a^2 \cos^2 \frac{\pi \delta \nu}{V} d\nu,$$

where a^2 is now a $f(\nu)$.

For simplicity, a band of finite width and uniform intensity lying between frequencies ν_1 and ν_2 may be examined, the middle of the band corresponding to ν_0 and a wave length λ_0. If one call $\lambda_1 - \lambda_2 = 2\epsilon$, λ_1 and λ_2 being the wave lengths corresponding to ν_1 and ν_2, one may write, since $\frac{V}{\lambda} = \nu$,

$$\frac{\nu_2 - \nu_1}{\nu_0} = \frac{\frac{V}{\lambda_2} - \frac{V}{\lambda_1}}{\frac{V}{\lambda_0}} = \frac{\frac{\lambda_1 - \lambda_2}{\lambda_1 \lambda_2}}{\frac{1}{\lambda_0}} = \frac{\lambda_1 - \lambda_2}{\lambda_0},$$

for λ_0^2 approaches $\lambda_1\lambda_2$. Hence

$$\frac{\nu_2 - \nu_1}{\nu_0} = \frac{2\epsilon}{\lambda_0}.$$

In the particular case considered, a^2 is constant with ν, and it is obvious that

$$\int I d\nu = 2a^2 (\nu_2 - \nu_1)\left[1 + \frac{\sin \frac{\pi\delta}{V}(\nu_2 - \nu_1)}{\frac{\pi\delta}{V}(\nu_2 - \nu_1)} \cos \frac{2\pi\delta}{V}\nu_0\right],$$

where the integration of the above expression for $Id\nu$ is taken from ν_1 to ν_2 with a constant. For finite values for $\nu_2 - \nu_1$, the intensity (when the cosine term is 1, for example) depends on the value of the factor $\alpha = \dfrac{\sin \frac{\pi\delta}{V}(\nu_2 - \nu_1)}{\frac{\pi\delta}{V}(\nu_2 - \nu_1)}$, which is now a function of δ. Hence $\int Id\nu$ is no longer independent of the value of δ in the cosine term alone, which is periodic, but it depends directly on a δ in the denominator of α. Thus, δ here does affect $\int Id\nu$. For values of δ small compared to λ_0 (*i.e.*, where $p = \dfrac{\delta}{\lambda_0}$ is a small number), the factor α does not differ sensibly from unity, for the product $\frac{\pi\delta}{V}(\nu_2 - \nu_1)$ is a small quantity, and the sine of such a quantity approaches the quantity. When, however, p increases so that the argument of the sine approaches π the quantity α vanishes, that is, the fringes vanish, for when the cosine term is 1 the whole term is very small, and the change in intensity from one maximum to a minimum is negligible. Before this occurs, that is to say, at any particular value of α, the interference fringes have an intensity which for the maximum is $1 + \alpha$ for the case where the argument of the cosine term is positive, and $1 - \alpha$ where it is negative, that is, there are variations in intensity at the points at which the fringes have a value of $1 + \alpha$ for the maxima and $1 - \alpha$ for the minima. If α is unity the contrast is great and fringes are visible and if α is 0 there is no contrast and they are invisible. Thus, viewing the fringes, it can be said that the

ratio of the minimum intensity in the fringes J_2 to the maximum intensity J_1 in the fringe system is given by

$$\frac{J_2}{J_1} = \frac{1 - \alpha}{1 + \alpha}.$$

Whence,

$$\alpha = \frac{J_1 - J_2}{J_1 + J_2}.$$

This quantity α was defined by Michelson as the *visibility* of the fringe. It is an arbitrary definition of what the eye would judge as the visibility formulated in terms of the parameter α of the above equation and the intensities. For $J_2 = 0$, $\alpha = 1$, and for $J_1 = J_2$, $\alpha = 0$. Thus α takes on values from 0 to 1 and the visibility of the fringes varies accordingly.

One may now turn to a study of the breadth of the spectral lines caused by the Doppler effect resulting from the distribution of velocities. This principle leads to the relation for the observed frequency ν relative to the emitted frequency ν_0 when the source moves towards the observer with a velocity u given by

$$\nu = \nu_0 \left(1 + \frac{u}{V}\right),$$

where V is the velocity of light. Thus, the relative variation of the frequency to a first approximation is $\frac{u}{V}$. If all the atoms have the same speed v, the width of the line would be simply $\nu_2 - \nu_1 = 2\frac{\nu_0 v}{V}$. Then, since, by the preceding deduction,

$$\frac{\nu_2 - \nu_1}{\nu_0} = \frac{2\epsilon}{\lambda_0} = \frac{2v}{V}, \text{ or } \frac{\epsilon}{\lambda_0} = \frac{v}{V}.$$

This band would have uniform intensity with sharp boundaries, since the molecular velocities are homogeneous in all directions. Thus the results of the preceding section are directly applicable and the visibility α takes the form,

$$\alpha = \frac{\sin 2\pi p \frac{v}{V}}{2\pi p \frac{v}{V}},$$

if it is remembered that $p = \frac{\delta}{\lambda_0}$, and that $\nu_2 - \nu_1 = \frac{2\nu_0 v}{V}$, and that $\frac{\nu_0}{V} = \frac{1}{\lambda_0}$.

The question arises, How does one subjectively judge the visibility, that is, under what conditions (*i.e.*, what value of α) do the fringes disappear? Lord Rayleigh arbitrarily decided that the limit of visibility was reached when $\frac{J_2}{J_1} = 0.95$. This estimate certainly is not far off, perhaps being a little high. It is, of course, subject to individual variations among the observers. Under these conditions α takes the value 0.025, or $\frac{1}{40}$. For this value of α the sin $2\pi p \frac{v}{V}$ is so nearly 0 that the product $2\pi p \frac{v}{V}$ must be nearly equal to π. This leads at once to an expression for the order of interference $p = \frac{\delta}{\lambda_0}$ given by $p = \frac{V}{2v}$, that is, in order that sin $2\pi p \frac{v}{V}$ be 0, p must be equal to $\frac{V}{2v}$. Hence $p = 0.5 \frac{\lambda_0}{\epsilon}$ when the fringes disappear. Now the average velocity of the molecules $\bar{c}$ is related to the temperature of the gas by

$$\bar{c} = v = \sqrt{\frac{8RT}{\pi M}}, \text{ for } \bar{c} = \sqrt{\frac{8}{3\pi}}\, C$$

and $C = \sqrt{\frac{3RT}{M}}$ by Sec. 42. Hence the breadth of the line ϵ is given by the relation

$$\frac{2\epsilon}{\lambda_0} = \frac{2v}{V} \text{ and } \frac{\epsilon}{\lambda_0} = \frac{\sqrt{\frac{8RT}{\pi M}}}{V} = A\sqrt{\frac{T}{M}},$$

where A is a constant $\frac{1}{V}\sqrt{\frac{8R}{\pi}} = 4.85 \times 10^{-7}$. Whence the limiting order of interference p is given by $p = 1.03 \times 10^{6}\sqrt{\frac{M}{T}}$.

This theory holds for the very simple case of all molecules having equal velocities. If, however, the Maxwellian distribution law holds, this must all be modified in accordance with the distribution. The distribution of velocities along the line of sight are in this case the only velocities which must be taken account of, for it is only in the line of sight that motion produces the Doppler effect. The number of atoms in a gas in equilibrium whose velocities lie between u and $u + du$ out of N atoms observed is given by the distribution law as $\eta_{du} = N\sqrt{\frac{hm}{\pi}}\, e^{-hmu^2}$

du by Sec. 43. This distribution of velocities leads to a change in frequency, such that for the atoms of velocity lying in an interval between u and $u + du$ there is a change in frequency $d\nu$ which is approximately equivalent to $\frac{u}{V}$. Since, however, the intensity of this light depends on n_{du}, and hence on u by the above relation, one may write that $a^2 d\nu = be^{-hmu^2} du$, where b is a constant depending on N and the other quantities involved as well as V. Since $\bar{c} = \frac{2}{\sqrt{\pi hm}}$ this becomes $a^2 d\nu = be^{-\frac{4u^2}{\pi\bar{c}^2}} du$. The distribution of intensity among the fringes is, therefore, found from

$$\int I d\nu = 4b \int_{-\infty}^{+\infty} \cos^2 \left[\frac{\pi\delta\nu_0}{V} \left(1 + \frac{u}{V} \right) \right] e^{-\frac{4u^2}{\pi\bar{c}^2}} du.$$

Since $2\cos^2 \left[\frac{2\pi\delta\nu_0}{V} \left(1 + \frac{u}{V} \right) \right] = 1 + \cos \left[\frac{2\pi\delta\nu_0}{V} \left(1 + \frac{u}{V} \right) \right]$

$$= 1 + \cos \frac{2\pi\delta\nu_0}{V} \cos \frac{2\pi\delta\nu_0 u}{V^2} - \sin \frac{2\pi\delta\nu_0}{V} \sin \frac{2\pi\delta\nu_0 u}{V^2},$$

the integration is simplified. As the last term is an odd function of u, it gives an integral 0, while the first two terms give well-known definite integrals. Hence

$$\int I d\nu = \pi b\bar{c} \left[1 + e^{-\pi\left(\frac{\pi p\bar{c}}{2V}\right)^2} \cos \frac{2\pi\delta\nu_0}{V} \right].$$

Here again it is seen that the quantity designated as α before (*i.e.*, the factor multiplying the cosine term) is given by

$$\alpha = e^{-\pi\left(\frac{\pi p\bar{c}}{2V}\right)^2}.$$

When p is small $e^{-\pi\left(\frac{\pi p\bar{c}}{2V}\right)^2}$ is close to unity and the visibility is good. If the Rayleigh value for limiting visibility of $\frac{J_2}{J_1} = 0.95$ or $\alpha = \frac{1}{40}$ is accepted, p for this case is given by

$$p = 0.690 \frac{V}{\bar{c}} = 1.42 \times 10^6 \sqrt{\frac{M}{T}}.$$

Fabry and Buisson, however, set the limiting visibility α as $\frac{1}{16}$, which gives a value of p the limiting order for visible fringes as

$$p = 1.22 \times 10^6 \sqrt{\frac{M}{T}}.$$

Thus comparing the Rayleigh value for p for the case of a broadening due to molecules all having the same velocity to one having a Maxwellian distribution, it is seen that p changes from 1.03 to 1.42. Thus the distribution law merely changes the value of the constant by a numerical factor which is of the order of 40 per cent.

The actual measurement of p was first made by Michelson and seemed to bear out the theory fairly well. The later results of Fabry and Buisson, however, seem to give an even more satisfactory agreement. The light from Geissler discharge tubes which were immersed in thermostated baths to keep T constant was analyzed by means of an interferometer. The difference of path of the interfering rays was then increased until the interference fringes ceased to be visible. This gave δ. The gases used were the inert gases, such as He, Ne, and Kr, as well as some ordinary gases like H_2. Under the conditions of the experiment the frequencies used came from lines known to have only a simple structure—that is, no complicated lines were chosen. Such lines come from the atoms of the elements, as is well known, for molecules give broad bands. Further experiments were made with the Geissler tubes immersed in liquid air to gain another value for T. M was given by the atomic weight of the gas. The value of p obtained from the value of δ at which interference fringes disappeared by dividing by λ_0 is given in column 4 of the table following. The calculated value of p from the values of M and T for the gases are given in the fifth column for room temperatures. For liquid-air temperatures the values of p' observed are given in the sixth column. The ratio of the value of p' observed at the liquid-air temperature to that at room temperature is given in the seventh column. The theoretical value for this, *e.g.*, $\sqrt{\frac{T}{T'}}$, is 1.73. Thus it seems as if the discharge warmed the gas slightly above the temperature of the bath.

Gas	Atomic weight	Wave length A°	Room temperature		Liquid-air temperature p' obs.	$\frac{p'}{p}$
			p obs.	p calc.		
He.........	4	5,876	144,000	144,000	241,000	1.66
Ne.........	20	5,852	324,000	321,000	515,000	1.60
Kr.........	83	5,570	600,000	597,000	950,000	1.58

The results show definitely the following facts: First, that p varies experimentally quite accurately as $\sqrt{M}$. Second, that it varies as $\sqrt{\frac{1}{T}}$ as accurately as the temperature conditions can be verified. Finally, p in order of magnitude agrees very well with the value computed from Maxwell's law. However, this agreement, which is within 1 per cent, is rather forced through the choice of $\alpha = {}^1\!/_{16}$. For $\alpha = {}^1\!/_{10}$, as suggested by Lord Rayleigh, the value would be about 14 per cent higher. Thus a complete verification of the law which depends on an accurate agreement between the constants can hardly be said to have been achieved. The much more certain proof of the law would result from a photometric comparison of the intensity of the fringes, *i.e.*, of $\frac{J_2}{J_1}$ and hence of α at different values of δ. This would give a complete and accurate verification of the law. It may again, however, be added that this work does definitely prove the existence not only of molecular velocities but of a distribution of velocities.

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CHAPTER V

THE MORE ACCURATE EQUATION OF STATE, OR VAN DER WAALS' EQUATION

47 Introduction. In the discussion of the gas laws on the basis of the kinetic theory, which has preceded this chapter, the molecules have for the most part been considered as points which have no forces acting between them. In the deduction of the expression for the mean free paths in Chap. III it became necessary to consider that the molecules have a volume, and use was made of a quantity b related to $\frac{4}{3}\pi r^3 N$, the total volume of the molecules present in a cm³. In fact, the pressure of a gas as calculated by Clausius in Sec. 19 made an allowance for such a term. As was shown in the second chapter, the kinetic hypothesis leads to the expression $pv = RT = \frac{1}{3}nmC^2$ for the type of gases postulated. This is commonly known as the Boyle's-Charles' law, and it holds true for the "permanent" gases under the experimental conditions usually employed in the common laboratory courses in physics, within the precision obtainable in such experiments. Even Boyle in his first measurements, however, noted that it did not hold rigorously, and stated the fact. As will presently be seen, accurate experiments show that this law does not hold at all accurately over large ranges and with a higher precision of measurement. The departures from this law, in part foreshadowed by Clausius in his theoretical treatment of the pressure relation, lead Van der Waals to his now famous equation of state. The development of the latter equation and its application to the interpretation of gaseous behavior will constitute the body of this chapter.

It should further be pointed out that, in turn, the Van der Waals' equation has its shortcomings. While in its present form it covers the general behavior of gases beyond the realms of Boyle's law satisfactorily for a large number of gases, it breaks down quite seriously when compared with still more accurate results. To replace it, various modifications or extensions have

been made to correct the errors introduced by the simplifying assumptions underlying it. Thus, while specifically Van der Waals' equation extends the Boyle's law equation by endowing molecules with volumes and forces, it assumes these volumes constant and the forces independent of the state of the gas. Actually, these conditions are not fulfilled and the extensions of the equation, some merely empirical in nature, attempt to correct this difficulty. They, in general, succeed in being of use for one set of phenomena involving the law, but none of them have the general applicability of the simpler equation. Necessarily, the better equations of this type reduce to the Van der Waals' equation in the limit when the factors causing the deviations from the equation are reduced to vanishingly small quantities. Again, the Van der Waals' equation itself reverts to the simple Boyle's-Charles' law when the molecular volumes and forces approach zero.

It is of interest to note in passing that the development of this law is a beautiful illustration of the progressive advance of physical science. First there is the discovery of a general regularity or law of nature through crude quantitative measurement. This is followed by a stimulating "explanation" in terms of a mechanical analogy. Then, as the result of more accurate measurements, what might be called second-order deviations come to light. Following these appears a brilliant *extension* of the mechanical theory to include the deviations. It is to be noted that such a change in the theory is not *revolutionary* in any sense. Nothing is upset and no errors have been made. The further investigation merely indicates the limitations of the fundamental assumptions. Such limitations being discovered, a further extension is possible, and the accuracy of the theory is extended perhaps to another significant figure. Following this improvement still more precise measurement again reveals deficiencies which require extension of the theory. Thus the knowledge and comprehension of the phenomenon can continue indefinitely, new improvements in technique making further experiment possible, new extensions in mathematical treatment also making perfection of the theory possible. It might seem as if this process could go on *ad infinitum.* Unfortunately, as accuracy advances progress becomes increasingly difficult, owing to the increase in mathematical complexity. Thus it soon becomes almost impossible to handle some of the resulting involved expressions. A simple example of this also appears in the practical application of the

equation of state. To this day most engineers are, for simplicity, forced to assume the Boyle's law equation, since the complications introduced by the more accurate Van der Waals' equation already begin to increase the complexity of their calculations more than the increase in accuracy would warrant.

The Van der Waals' equation, accordingly, besides furnishing an admirable second approximation to the true behavior of gases, can be of value in indicating the manner of advance of scientific thought. From what has preceded, it is seen that, while it has its limitations, it is perhaps the most serviceable equation, for, owing to its still considerable simplicity, it makes it possible to deduce the values of the constants involved (*e.g.*, the size of the molecules and the constant of attraction) to a first order of approximation. With the more accurate modifications the increasing complexity of the quantities render such evaluations more difficult, and the loss of generality in application renders correlation between the constants of the equation obtained from a variety of phenomena impossible. Thus by its means, as will be seen in this chapter, the molecular constants a and b can be determined and can be found to agree from three apparently independent sets of data, to wit: (1) deviation from the gas laws, (2) critical constants, (3) the Joule-Thomson effect.

48. Deviations, from Boyle's Law and the Deduction of Van der Waals' Equation. If the product $pv = RT =$ constant is plotted as ordinates against p, the pressure, as abscissæ, the resulting curve should be a straight line parallel to the axis of abscissæ as long as Boyle's law holds. This is shown in curve 1, Fig. 24. There are, however, no gases for which this is true if the measurements are accurately made. For the gases H_2 and He the product pv plotted against p gives nearly a straight line, which rises gradually as p increases. The behavior for these gases is seen in curve 2, Fig. 24. For most gases, however, the curve for the product pv at first falls below pv equals a constant as p increases, and later rises above this line. For O_2 and N_2 the decrease is slight, while for the more condensible gases the initial drop is more pronounced. Such a curve is shown in curve 3, Fig. 24.

The explanation of these phenomena is qualitatively simple. In the first place, if Clausius' deduction of the pressure relation which allows for the volume of the molecules is correct (Sec. 19), *i.e.*, if $p(v - b) = RT = \frac{1}{3}m\nu C^2$, then $pv - pb = RT$, or, better,

$pv = RT + pb$. Thus, as p increases pv *increases* linearly with it. Its rate of increase is then determined by b, the coefficient of p, and the greater b the more rapid the rise. This b is nothing but a function of the volume of the molecules, which was taken as four times the total volume of the molecules present in the volume v of the gas, so that it should be possible from such deviations to evaluate b and hence the size of the molecules. Thus the deviations of the type-2 curve is satisfactorily explained by taking account of the volumes of the molecules. The initial fall of the curves of the third type in Fig. 24, however, still requires explanation. This curve demands that, as p increases, the product pv must first decrease, that is, v must decrease *more*

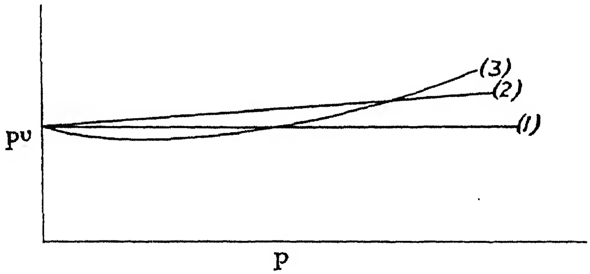

FIG. 24.

rapidly than p increases. Such a change in v can only take place if some pressure other than p is active in changing the volume. Now the fact that molecules condense to form a liquid or a solid under the proper conditions indicates very definitely that the molecules attract each other. Thus the forceless molecules previously assumed must for all gases be replaced by molecules which attract each other. If this be assumed to be the case, and if it be further assumed that the attractive forces of the molecules extend over limited distances only, then the more molecules there are in a given volume the greater will be the attraction. Hence it would be expected that, as the volume decreases, the internal pressure due to the attractions of the molecules would increase. Thus it is to be expected from the behavior of the pv-p curves that, besides the external pressure p on a gas, there is an internal pressure p' due to mutual attraction of the molecules. This pressure p' is a function of the volume of the gas and must be added to p in any correct gas-law equation.

Van der Waals, in 1880, had the insight to derive an expression for the value of this pressure p' and thus to deduce an equation of

state which stands today as the most *generally* satisfactory approximation to the gaseous behavior. His evaluation of the pressure p' was based on an analogy to Laplace's famous equation of surface tension. Surface tension is again a phenomenon due to the mutual attraction of molecules, and hence it is not surprising that the type of reasoning successful in one case should be equally successful in a similar case. If one considers the outer layer of gas in a containing vessel, one notes first the external pressure p on this layer exerted by the walls. If, however, the gas molecules attract each other, those on the outside will not be attracted outward, as there is no gas present to attract them. They will, however, suffer an attraction inward by all inward lying molecules. Now it is obvious that the attractive forces of molecules on other molecules must vary with the distance. Hence it is conceivable that molecules lying far away from a given molecule will suffer negligible attraction from it. It must, accordingly, be assumed that, in general, there is a distance x in a gas beyond which the attraction of one molecule for another is negligible. What the magnitude of this distance is is not of material importance for the present discussion. It must exceed the average distance between the molecules in a gas to be effective at all. Probably it is of the order of a number of mean free paths at N.T.P. One can, therefore, consider a layer of gas x cm thick, over the outer surface of the gas, in which each molecule has an inward component of force exerted on it by the molecules lying within x cm interior to it, for the inward components of force on these molecules are not balanced by outward components of force, since there are no molecules more than x cm outside of this layer to attract them.* Since the force on the layer is due to the molecules, it must be proportional to the number of molecules in it. The smaller the volume in which a given number of molecules are confined the greater the number of molecules that find themselves in this layer of thickness x. Thus since decreasing the volume v in which the n molecules are confined increases the number n' in the surface layer proportionally to $\frac{1}{v}$, the force which is exerted by the interior molecules on

* There are, of course, forces exerted on the molecules by the walls of the containing vessel. These are, however, negligible compared to the forces between the molecules themselves and so may be neglected here. The cause for this may be seen in the nature of the adsorbed-gas molecules on the walls (see Sec. 84, Chap. VII).

the surface layer will be increased in proportion to n', that is, to $\frac{1}{v}$. But, again, since decreasing v also changes the number of molecules n in the interior of the gas, which are close enough to the outer layer x cm thick to act on the molecules in it, in the proportion of $\frac{1}{v}$, the total resultant force, must be proportional to $\frac{1}{v^2}$, that is, since the number of attracted molecules in the outer layer x and those inside coming close enough to x to attract them are both increased in proportion to $\frac{1}{v}$, the resultant increase in force on the surface layer must be proportional to $\frac{1}{v^2}$ and one may write $p' = \frac{a}{v^2}$, where a is a constant of proportionality. It is obvious that a must be a constant characterizing the attractive forces for each particular kind of gas, and should be independent the volume v of the gas. Thus the equation properly describing the behavior of a gas must contain both the correction for the volume of the molecules and for the value of the internal pressure. Thus Van der Waals' equation may be written

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT = \frac{1}{3}\, nmC^2.*$$

It is this equation which, in general, most conveniently fits the behavior of a gas to a second degree of approximation. By its application to gaseous behavior the values of a and b may be found for different gases.

Thus in the explanation of the curves of type 3 of Fig. 24, which was discussed, the equation takes the form

$$pv = RT + pb - \frac{a}{v} + \frac{ab}{v^2}.$$

Since a and b are both small $\frac{ab}{v^2}$ is a small quantity of higher order and may be neglected. Hence the expression for the quantity pv becomes $pv = RT + pb - \frac{a}{v}$. This equation very satis-

* The n here used represents the molecules in the volume v. It will hereafter be used in place of the ν formerly used.

factorily explains the initial drop of the pv curve as p increases. For if a is greater than b, as v decreases the $\frac{a}{v}$ term increases more rapidly than pb increases. It seems as if the resulting decrease of pv should go on indefinitely. As the pressure goes still higher, however, the volume becomes so small that the molecules become crowded together and the spaces between them become of the same order of magnitude as the molecules themselves. When this point is reached, further changes in p produce comparatively small changes in v (*i.e.*, $\frac{1}{v}$ is no longer proportional to p). Thus the pb term increases more rapidly than the $\frac{a}{v}$ term and soon becomes the important factor causing the curve to rise again. With H_2 and He, however, the a is so small as to cause little or no change in the slope of the curve due to pb, and the type-2 curves result. Hence one may already qualitatively see the differences in gaseous behavior due to a difference in the constant a.

49. Note on the Value of Van der Waal's b. In Chap. III it was shown that each molecule excluded the centers of all the molecules considered as points from a volume $\frac{4}{3}\pi\sigma^3$, where $\sigma = 2r$, r being the radius of the molecules. It was pointed out, however, in Sec. 19 that, since the point molecule was able to strike but one hemisphere of the sphere of action of a molecule with which it collided, the real volume from which every other molecule was excluded was not $\frac{4}{3}\pi\sigma^3$, but just one-half of this, that is $\frac{2}{3}\pi\sigma^3$. Thus the volume available for free motion was $V - b$, where $b = \frac{2}{3}\pi\sigma^3 n$. This value of b gave a correction term to the mean free path, which for rarefied gases (*i.e.*, all common cases of application) could be neglected. Since, however, the b is of great importance in Van der Waal's equation and can be of service in determining r, the radius of the molecules, it demands a more complete discussion.

The value of b above may be deduced a little differently. A simple deduction of the equation for the mean free path was given in Sec. 16. In this case L was found to be equal to $\frac{V}{\frac{4}{3}\pi\sigma^2 n}$ if

the correction for relative velocity were added. Here n is the number of molecules in the volume V. This deduction assumed that the molecule acted like a disc of radius σ. In impact, however, if the molecules have volumes, then the impact must occur at values of L less than this. Consider spherical molecules with a radius r colliding. If the collision be head on as in (b), Fig. 25, the length of path will not be L as in (a) Fig. 25 for disc-like molecules, but $L - \sigma$, where $\sigma = 2r$. But impacts of the type shown in (c), Fig. 25, may also occur. Hence L will

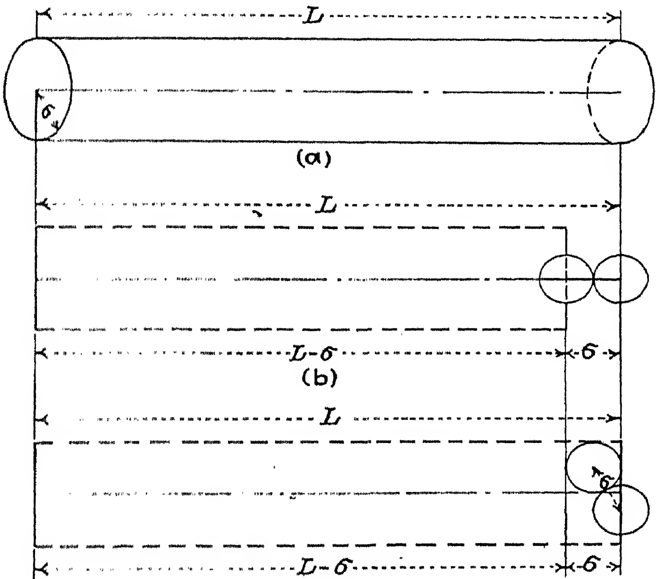

Fig. 25.

take on a value between $L - \sigma$ and L. Now the quantity required is the average value for this decrease. This can be found as follows: Impacts, according to Van der Waals, are equally probable on any portion of the surface of the sphere of exclusion of radius σ drawn about the fixed molecule. One may then ask what the average distance of approach in collisions of this type would be. If n molecules impinge per cm² on a spherical surface, then the number impinging on a zone of width $\sigma d\theta$ and radius $a = \sigma \cos \theta$ (see Fig. 26) will be $2\pi n\sigma^2 \cos \theta d\theta$. The distance of approach for the impact characterized by this zone at the

angle θ is $\sigma \sin \theta$. Hence the average distance of approach is given as

$$\bar{x} = \frac{\int_0^{\frac{\pi}{2}} n 2\pi\sigma^3 \sin\theta \cos\theta d\theta}{2\pi\sigma^2 n},$$

where $2\pi\sigma^2 n$ is the number impinging on the whole hemisphere. Solving this equation, $\frac{\sigma}{2}$ is obtained as the value by which L is shortened. For a disc-like molecule the free path was

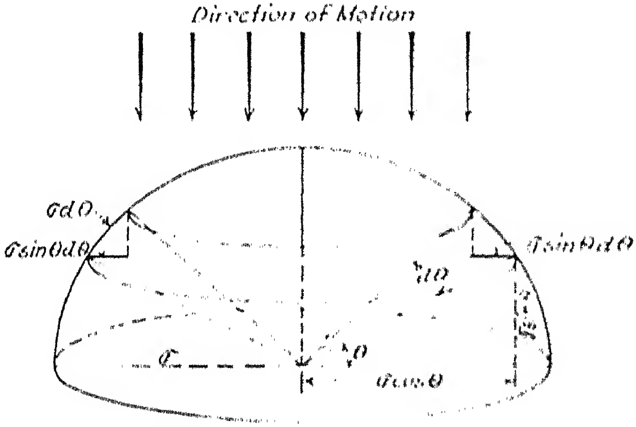

FIG. 26.

taken as $L_d = \frac{V}{\frac{4}{3}\pi\sigma^2 n}$. For a spherical molecule, accepting the assumptions of Van der Waals, mentioned above,

$$L_s = L_d - \frac{\sigma}{2},$$

Thus
$$\frac{L_s}{L_d} = 1 - \frac{\sigma}{2L_d} = 1 - \frac{\frac{\sigma}{2}\left(\frac{4}{3}\pi\sigma^2 n\right)}{V}$$

$$= \frac{V - \frac{2}{3}\pi\sigma^3 n}{V},$$

This change in L is due to the volume of the molecules and must yield b. Hence the $V - b$ which must be included for such molecules as have a real volume is given by $b = \frac{2}{3}\pi\sigma^3 n$ or $b = \frac{2}{3}$

$(8\pi r^3 n) = 4\left(\frac{4}{3}\pi r^3 n\right) = 4\omega$, where ω is the volume of all the molecules in the space. This is the same value for b found from very simple considerations in Sec. 20.

This argument contains one fallacy, as Van der Waals himself later recognized. The impacts on the hemispherical surface were in the deduction above taken as equally probable. This is in error, since the Fig. 25 is drawn so that the shortening of the free path is along the line of motion only. Thus the impacts are not equally probable over the surface of the hemisphere about the end molecule. They are really equally probable over the base of the hemisphere, which is perpendicular to the direction of motion. The average must, accordingly, be taken as follows: If n molecules strike a cm² of surface at right angles to the motion, the number striking the zone $\sigma d\theta$, of radius $\sigma \cos \theta$, is not $2\pi n\sigma^2 d\theta \cos \theta$ as before, but the projection of this at right angles to the motion, *i.e.*, $2\pi n\sigma^2 \sin \theta \cos \theta d\theta$. The average distance of approach is, then, this quantity multiplied by the distance of the zone from the base of this hemisphere, that is, by $\sigma \sin \theta$, integrated from 0 to $\frac{\pi}{2}$ and divided by n times the *base of the hemisphere*. Thus the average value is not $\bar{x}$ as before, but $\bar{x}'$ given by

$$\bar{x}' = \frac{\int_0^{\frac{\pi}{2}} 2\pi n\sigma^3 \sin^2 \theta \cos \theta d\theta}{\pi\sigma^2 n} = \frac{2}{3}\sigma.$$

Hence $L_s = L_d - \frac{2}{3}\sigma$ and $\frac{L_s}{L_d} = 1 - \frac{2\sigma}{3L_d} = 1 - \frac{\frac{2\sigma}{3}\left(\frac{4}{3}\pi\sigma^2 n\right)}{V}$

$$= \frac{V - \frac{8}{9}\pi\sigma^3 n}{V} = \frac{V - \frac{16}{3}\left(\frac{4}{3}\pi r^2 n\right)}{V}.$$

Thus $b = \frac{16}{3}\omega = 5.33\omega$ instead of 4ω as Van der Waals assumed. Neither this deduction nor the one preceding assumed a Maxwellian distribution of velocities. In both expressions the correction for a relative velocity with molecules having equal speeds was used.

According to O. E. Meyer,[1] Van der Waals later altered his average distance of approach in conformity with this correction.

In doing so he also extended the correction to take care of Maxwell's distribution of velocities and the fact that both molecules were moving. Calculations for which there is no place in this text give the change in L under these conditions as the quantity $L_s = L_d - \frac{\sqrt{2}}{3}\sigma$. In this case the quantity L_d from the Maxwellian distribution of velocities must be used. This quantity, it will be remembered, was $\frac{V}{\sqrt{2}\pi\sigma^2 n}$ (Sec. 37), the $\sqrt{2}$ being introduced by the value of the average relative velocity. Hence

$$\frac{L_s}{L_d} = 1 - \frac{\frac{\sqrt{2}}{3}\sigma}{L_d} = 1 - \frac{2}{3}\frac{\pi\sigma^3 n}{V} = \frac{V - 4\left(\frac{4}{3}\pi r^3 n\right)}{V}.$$

Hence $b = 4\omega$, as Van der Waals originally found. Thus the most correct value of b from this type of consideration is $b = 4\omega$. It is a strange coincidence that this value for b should agree with Van der Waals' originally erroneously deduced value.

Starting from an entirely different type of considerations, neglecting relative velocities and distribution of velocities, R. Clausius[2] and Jaeger[3] independently arrived at a different value for b. Jaeger's deduction is more formal and of a general nature. It makes use of a new idea involved in the nature of elastic impacts.[4] That of Clausius is a direct consequence of the general value for the mean free path deduced in Secs. 16, 17, and 19, and merits being given.

It was there found that $L = \frac{4U}{S}$, where U is the total available volume and S the surface against which the molecules impacted. U was at that point taken as $V - b$. In this consideration $b = \frac{4}{3}\pi\sigma^3 n$ can properly be called the total volume from which each molecule is excluded. The quantity σ is, as before, $2r$, where r is the radius of a molecule. Hence $U = V\left(1 - \frac{\frac{4}{3}\pi\sigma^3 n}{V}\right)$. Now Clausius points out that the surface S is not $4\pi\sigma^2 n$, the total surface of all the spheres of exclusion. It is less than this, for it often occurs that many of the molecules are so

close together that their fields of exclusion overlap while the molecules are still separate. These then cut out the overlapping parts of their surfaces from the available surface for impact. Thus from $4\pi\sigma^2 n$ must be deducted the area S' of all the n surfaces of the spheres of exclusion which are overlapping. These are unavailable for usual impacts, as a triple collision is very rare. The value of S' can be readily calculated. An overlapping takes place for all molecules in which the distance between the centers is less than 2σ but not less than $\sigma = 2r$, for no two molecules can come closer than $2r$. Call a any length between σ and 2σ, that is, $\sigma < a < 2\sigma$. The chance that the center of one molecule lies between a and $a + da$ from another is then simply the ratio of the

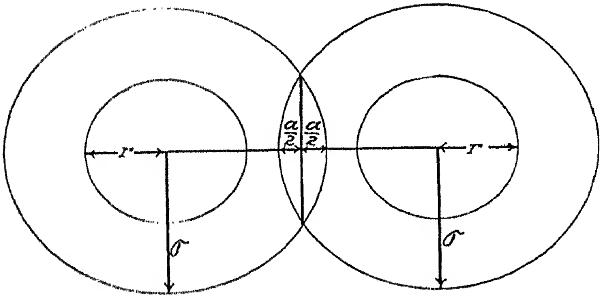

FIG 27.

volume $4\pi a^2 n da$ to V, the total volume available, *i.e.*, $P_{da} = \frac{4\pi a^2 n da}{V}$. If, now, two of the molecules are a cm apart their spheres of action intersect each other and the plane of the circle of contact is $\frac{1}{2}a$ from the center of each (see Fig. 27). The altitude of the section of this sphere above this plane is $\sigma - \frac{1}{2}a$. The surface of this intercepted portion of the sphere of action which ceases to be effective in collisions is then $2\pi\sigma\left(\sigma - \frac{1}{2}a\right)$. Thus for the n molecules the surface given by the integral of the product of $2\pi\sigma\left(\sigma - \frac{1}{2}a\right)$ and the probability P_{da} from $a = \sigma$ to $a = 2\sigma$, to wit

$$S' = \frac{n^2\pi^2\sigma}{V}\int_{\sigma}^{2\sigma}\left(\sigma a^2 - \frac{1}{2}\, a^3\right)da$$

is the surface which must be subtracted from the whole surface of the molecules present, against which impact can take place. The value of this integral is $\frac{11}{3}n^2\frac{\pi^2\sigma^5}{V}$. Thus the surface available for impact is

$$S = \sum - S' = 4\pi\sigma^2 n - \frac{11}{3}n^2\frac{\pi^2\sigma^5}{V} = 4\pi\sigma^2 n\left(1 - \frac{11}{16}\frac{\frac{4}{3}\pi n\sigma^3}{V}\right).$$

Since in Sec. 17 the value of L was set equal to $L = \frac{4V}{S}$,

$$L = \frac{4V\left(1 - \frac{\frac{4}{3}\pi\sigma^3 n}{V}\right)}{4\pi n\sigma^2\left(1 - \frac{11}{16}\frac{\frac{4}{3}\pi n\sigma^3}{V}\right)}.$$

On division through by $\frac{4}{3}\pi n\sigma^3$ and neglect of higher orders of this term than the first, the equation yields

$$L = \frac{V}{\pi n\sigma^2}\left[1 - \frac{\frac{5}{16}\left(\frac{4}{3}\pi n\sigma^3\right)}{V}\right],$$

whence $b = \frac{5}{2}\left(\frac{4}{3}\pi n r^3\right) = 2.5\omega$. This correction was made independently of any assumption of the velocities of the molecules. Therefore the relative velocity correction term in L must be added as it was in Chap. III. In order to do this it must, however, be assumed that the relative velocities do not change the surface S exposed. This is obviously not correct. The relative velocities would increase the chance of encounter and hence increase the value of b. In a more recent book Jaeger[a] used Van der Waals' later value $b = 4\omega$ in place of the value 2.5ω of Clausius and himself. As will later be seen in the derivation of Van der Waals' equation from the theorem of the virial by H. A. Lorentz (Sec. 50), the value of b found comes out as 4ω. Since this is a very rigorous deduction it may be assumed to be correct. Accordingly, it seems that the value of $b = \frac{2}{3}\pi n\sigma^3$ given by Van der Waals is the most reliable value, and it is the one most frequently used today. It must be added, however, that too great a reli-

ability cannot be placed on the exact numerical value of the factor 4, as is seen by these considerations. This place offers an example of a deficiency in the kinetic theory which too frequently occurs. In the type of statistical discussion appearing in the theory it can happen that frequently two different viewpoints will lead to entirely different processes of averaging. Such processes yield different values of the numerical constants, and it is sometimes impossible at the present state of knowledge to decide which mode of averaging is the correct one. One is therefore frequently hampered in checking the theory experimentally by a considerable uncertainty in the values of the constant terms. Thus the striking numerical agreements between theory and experiment which should be possible are occasionally vitiated by uncertainties of the values of constant coefficients which may reach many per cent.

50. Deduction of Van der Waals' Equation from the Theorem of the Virial.—A more rigorous and perhaps more satisfying deduction of Van der Waals' equation comes from a consideration of Clausius'[6] well-known Theorem of the Virial. As it is not readily accessible to the reader, it may not be out of place to discuss it at this point.

It is first necessary to deduce the theorem of the virial in order to understand its function. The derivation here used is taken from the admirable treatment of Clemens-Schaefer.[7] Let it be assumed that the equations of dynamics may be applied to the centers of gravity of each of the molecules of mass m of a homogeneous gas. Then one can write for the equations of motion of these molecules

$$m\frac{d^2x}{dt^2} = X,\ m\frac{d^2y}{dt^2} = Y, \text{ and } m\frac{d^2z}{dt^2} = Z.$$

In these equations the coordinates of the molecule along the three axes are x, y, and z, while X, Y, and Z are the three components of the external forces acting on the molecule. Multiplying these equations through by x, y, and z, respectively,

$$mx\frac{d^2x}{dt^2} = Xx,\ my\frac{d^2y}{dt^2} = Yy,\ mz\frac{d^2z}{dt^2} = Zz.$$

Since, however, the quantity $mx\frac{d^2x}{dt^2}$ may be expressed by

$$mx\frac{d^2x}{dt^2} = \frac{d^2\left(\frac{m}{2}x^2\right)}{dt^2} - m\left(\frac{dx}{dt}\right)^2,$$

and similarly for the y and z components, these equations of motion may be written in the following fashion:

$$\frac{d^2\left(\frac{mx^2}{4}\right)}{dt^2} - \frac{m}{2}\left(\frac{dx}{dt}\right)^2 = \frac{1}{2}Xx.$$

$$\frac{d^2\left(\frac{my^2}{4}\right)}{dt^2} - \frac{m}{2}\left(\frac{dy}{dt}\right)^2 = \frac{1}{2}Yy.$$

$$\frac{d^2\left(\frac{mz^2}{4}\right)}{dt^2} - \frac{m}{2}\left(\frac{dz}{dt}\right)^2 = \frac{1}{2}Zz.$$

Adding these quantities together,

$$\frac{m}{4}\frac{d^2}{dt^2}(x^2 + y^2 + z^2) - \frac{m}{2}\left[\left(\frac{dx}{dt}\right)^2 + \left(\frac{dy}{dt}\right)^2 + \left(\frac{dz}{dt}\right)^2\right] = \frac{1}{2}(Xx + Yy + Zz).$$

This equation applies to one molecule, and it must now be summed up for all molecules of the gas. Thus,

$$\frac{m}{4}\sum\frac{d^2}{dt^2}(x^2 + y^2 + z^2) - \frac{1}{2}\sum mc^2 = \frac{1}{2}\sum(Xx + Yy + Zz).$$

This equation can now be multiplied by an elementary time interval dt and integrated over a comparatively long time interval τ.*

$$\frac{m}{4}\sum\int_0^\tau\frac{d^2}{dt^2}(x^2 + y^2 + z^2)dt - \sum\int_0^\tau\frac{m}{2}c^2dt = \frac{1}{2}\sum\int_0^\tau(Xx + Yy + Zz)dt.$$

Dividing this quantity by τ,

$$\frac{m}{4\tau}\sum\left|\frac{d}{dt}(x^2 + y^2 + z^2)\right|_0^\tau - \frac{1}{\tau}\int_0^\tau\frac{m}{2}c^2dt = \frac{1}{2\tau}\sum\int_0^\tau(Xx + Yy + Zz)dt.$$

If, now, the values of all velocities and coordinates are conceived of as remaining within finite limits, then for a relatively large τ the first term will become vanishingly small while the others remain finite, for the first term is divided by τ but contains no τ while the other terms contain τ as well as being divided by τ.

* This time interval need be long only in the sense of the average times between disturbances of the motion of a molecule. Since the mean free path is of the order of 10^{-5} cm and $\bar{c}$ is of the order of 10^4 cm/sec., the time for such an occurrence is 10^{-9} sec. Hence for the integration in question τ need not be a great fraction of a second.

The ~~first~~ II term that does not vanish under the above conditions is nothing but the total kinetic energy of agitation of the molecules, averaged over a finite time. This may be written $\overline{\sum \frac{m}{2} c^2}^t$. The term on the right-hand side of the equation is the average value of the sum $\frac{1}{2}\sum(Xx + Yy + Zz)$, taken over a finite time interval, and it can be written as $\frac{1}{2}\overline{\sum(Xx + Yy + Zz)}^t$. Now the quantity $\overline{\sum \frac{m}{2} c^2}^t$ is really nothing but the average total kinetic energy of the molecules present in a given volume, to wit $\frac{1}{2}nmC^2$, where n is the number of molecules present.

Then the equation becomes

$$\frac{1}{2}nmC^2 + \frac{1}{2}\overline{\sum(Xx + Yy + Zz)}^t = 0.$$

The quantity $-\frac{1}{2}\overline{\sum(Xx + Yy + Zz)}^t$ was called by Clausius the "virial" of the mechanical system; and the above equation states that the total kinetic energy of the system is equal to the virial of the same. This constitutes the famous theorem of the virial.

This theorem may at once be applied to deduce the expression for the equation of an ideal gas. Consider the gas enclosed in a parallelopiped of volume $V = abc$, the sides a, b, and c being parallel to the coordinate axes. For the ideal gas, no forces act between the molecules at all and merely the forces experienced by the molecules in impact with the walls need be regarded. Consider the two walls of the paralellopiped which lie parallel to the yz-plane, the one wall having the x coordinate equal to 0, the other wall the x coordinate equal to a. Now, denote the time average of the force on the wall per unit area by p. For the wall at $x = 0$, p is in the direction of the positive x-axis; for the wall at $x = a$, it is in the direction of the negative x-axis. Thus for the first-named wall $\sum\left(\overline{Xx}^t\right)_{x=0} = +\,pbc\,0 = 0$, and for the second-named wall $\sum\left(\overline{Xx}^t\right)_{x=a} = -pbca = -pV$. Exactly the same value is obtained for each of the other two pairs of walls, whence $-\frac{1}{2}\sum\overline{(Xx + Yy + Zz)}^t = \frac{3}{2}pV$. Thus the theorem of the virial at once gives $\frac{3}{2}pV = \frac{1}{2}nmC^2$, or $p = \frac{1}{3}\frac{nmC^2}{V} = \frac{1}{3}NmC^2$.

This is the simple equation for an ideal gas which was deduced in a very elementary fashion in Sec. 5.

It now becomes necessary to carry this deduction over to the case of the non-ideal gas. This treatment is also taken from the admirable text of Clemens-Schaefer.[11] In this case intermolecular forces act on the gas molecules beside the forces assumed above, *i.e.*, those of the walls. These forces must be taken account of in the virial.

Let it be assumed that the molecules *are hard elastic spheres between which forces act which are functions of the distances between the molecules. Let it be further assumed that these forces decrease rapidly to* 0 when the distances between the molecules exceed a certain value. Call $\phi(r)$ the force between two molecules located at the points x, y, z, and x', y', z'. It then follows that r, the distance between them, is given by $r^2 = (x - x')^2 + (y - y')^2 + (z - z')^2$. The force components X, Y, Z and X', Y', Z' acting on these molecules are then given by the following relationships:

$$X = \phi(r)\frac{x - x'}{r} \qquad X' = \phi(r)\frac{x' - x}{r}$$
$$Y = \phi(r)\frac{y - y'}{r} \qquad Y' = \phi(r)\frac{y' - y}{r}$$
$$Z = \phi(r)\frac{z - z'}{r} \qquad Z' = \phi(r)\frac{z' - z}{r}$$

(*i.e.*, they are the projections of $\phi(r)$ on the X-, Y-, and Z-axes). The unaveraged virial for these two molecules thus becomes

$$-\frac{1}{2}\left[\left\{\phi(r)\frac{x - x'}{r}x - \phi(r)\frac{x - x'}{r}x'\right\} + \left\{\phi(r)\frac{y - y'}{r}y - \phi(r)\frac{y - y'}{r}y'\right\} + \left\{\phi(r)\frac{z - z'}{r}z - \phi(r)\frac{z - z'}{r}z'\right\}\right].$$

On rearranging these terms one arrives at the relation

$$-\frac{1}{2}\frac{\phi(r)}{r}[(x - x')^2 + (y - y')^2 + (z - z')^2] = -\frac{1}{2}r\phi(r).$$

Therefore the unaveraged virial for all the molecules for these forces is simply $-\frac{1}{2}\sum\sum r\phi(r)$. The double summation is carried out for all pairs of molecules. This correction for attractive forces must be added to the virial term deduced above

for the pressure of the walls in the case of an ideal gas. The equation therefore becomes in this case

$$pV = \frac{1}{3}nmC^2 - \frac{1}{3}\sum\sum r\phi(r).$$

The averaging over a given time interval may be left out for the last term, for $\sum\sum r\phi(r)$ is a constant for the equilibrium condition which is being dealt with.

It is now necessary to determine the value of $\sum\sum r\phi(r)$. To this end the action between a single molecule with the molecules lying in a volume $d\tau$ at a distance r may be considered. In this volume, on the average, there are $dn = \frac{n}{V}d\tau$ molecules, so that the force between this element and a single molecule is given by $\frac{n}{V}\phi(r)rd\tau$. Changing to polar coordinates, $d\tau = r^2dr \sin\theta d\theta d\phi$, and one has the force given by $\frac{n}{V}\phi(r)r^3dr \sin\theta d\theta d\phi$. If in place of the single molecule considered, one regards the molecules in a small volume $d\tau'$, in which there are $\frac{n}{V}d\tau'$ molecules taken at the point where the single molecule was, one has for the force between $d\tau$ and $d\tau'$ the quantity $d\tau'\frac{n^2}{V^2}\phi(r)r^3dr \sin\theta d\theta d\phi$. To get the whole force, these volumes must be integrated for $d\tau'$ as well as for $d\tau$. The result must however, be divided by 2, since otherwise the whole volume would be taken twice. Thus

$$\sum\sum r\phi(r) = \frac{1}{2}\frac{n^2}{V^2}\int d\tau'\int \phi(r)r^3dr \sin\theta d\theta d\phi$$
$$= \frac{2\pi n^2}{V^2}\int d\tau'\int_\sigma^\infty \phi(r)r^3dr.$$

Since $\phi(r)$ was assumed to decrease rapidly with r, it is possible to integrate r from σ† to infinity instead of integrating only over values corresponding to the volume V.* This integral is therefore a

* This assumption is the same one contained in the other derivation of Van der Waals' equation. The latter assumed that the law of force was such that the force between molecules *fell to zero for distances considerably less than the dimensions of the vessel* (*i.e.*, that the radius of the sphere of action was small compared to the dimensions of the containing vessel).

† σ is here sum of radii of the two molecules.

constant. The integral of $d\tau'$ gives only the volume V. Therefore

$$\frac{1}{3}\sum\sum r\phi(r) = \frac{2\pi n^2 V}{3}\frac{}{}\int_\sigma^\infty \phi(r)r^3\,dr.$$

Or setting

$$\frac{2}{3}\pi n^2\int_\sigma^\infty \phi(r)r^3\,dr = a,$$

then

$$\frac{1}{3}\sum\sum \phi(r)r = \frac{a}{V^2}V.$$

Thus the expression for the pressure assuming forces of attraction becomes

$$\left(p + \frac{a}{V^2}\right)V = \frac{1}{3}nmC^2.$$

This equation has so far taken the proper account of the pressure contribution to the equation of state; it does not, however, contain the correction for the volume of the molecules. The effect of these molecules on the virial is to add repulsive forces at the surfaces of the molecules. The calculation of the effect of these was first carried through by H. A. Lorentz.

This part of the virial may be called the repulsive virial, and it may be designated by R. At the instant of impact let it be assumed that the molecules at a distance σ of each other exert a force $k_1 = k_2$ each on the other. The repulsive viral thus has the value $\frac{1}{2}k\sigma$ for the pair. The total virial is obtained by summing over all pairs of molecules for a sufficient time τ and dividing by τ. Thus it has the value

$$R = -\frac{1}{2\tau}\int_0^\tau \sum (k\sigma)dt = -\frac{\sigma}{2\tau}\int_0^\tau \sum k\,dt.$$

An interchange of the order of summation and integration leads to the relation

$$R = -\frac{\sigma}{2\tau}\sum\int_0^{\tau'} k\,dt.$$

Now the force k acts only during the time of impact, and τ' is therefore merely this time of impact. Thus the $\int_0^{\tau'} k\,dt$ is the time integral of the force, that is to say, the impulse given the molecule. Thus if C_r is the relative velocity of the molecules and C_{r_n} the component of this normal to the tangential plane at impact, then, in impact, this quantity alone is changed. The

momentum transfer is thus $\int_0^\tau kdt$, which equals mC_{r_n}, the momentum change. The truth of this is at once obvious, for it is well known that equal molecules of mass m, if one be considered at rest and the other moving relative to it with a velocity C_r, suffer a change in momentum along the normal to the tangential plane at impact only (see Sec. 28). This change is equal to a change in momentum from mC_{r_n} to 0 for the moving molecule, and from 0 to mC_{r_n} for the one at rest. Thus one may write for $R = -\frac{m\sigma}{2\tau}\sum C_{r_n}$ summed up over all pairs of molecules which collide during the time τ. Now this summation of all the molecules colliding in a time τ can most easily be performed by a consideration of the α type of impact discussed in Chap. IV, Sec. 27. In Sec. 27 of the chapter on Maxwell's distribution of velocities the number of collisions per second of molecules whose velocity components lay between u and $u + du$, v and $v + dv$, w and $w + dw$ with molecules of velocities lying between u' and $u' + du'$, v' and $v' + dv'$, and w' and $w' + dw'$ was shown to be given by the expression*

$$\nu_\alpha = N^2\frac{\beta^6}{\pi^3}e^{-\beta^2(c^2+c'^2)}\sigma^2C_r \cos \theta dkdudvdwdu'dv'dw'.$$

Since $N = \frac{n}{V}$, and multiplying by τ,

$$\nu_\alpha\tau = \frac{n^2}{V^2}\frac{\beta^6\tau}{\pi^3}e^{-\beta^2(c^2+c'^2)}\sigma^2C_r \cos \theta dkdudvdwdu'dv'dw'.$$

* ν_a was in Sec. 27 shown to be given by

$$\nu_a = F(u, v, w)F(u', v', w')\delta^2C_r \cos \theta dkdudvdwdu'dv'dw'.$$

From Sec. 31 it was found that $F(u, v, w)$ and $F(u'v'w')$ were expressed as

$$\frac{N}{\alpha^3\pi^{\frac{3}{2}}}e^{-\frac{u^2+v^2+w^2}{\alpha^2}} \text{ and } \frac{N}{\alpha^3\pi^{\frac{3}{2}}}e^{-\frac{u'^2+v'^2+w'^2}{\alpha^2}}$$

whence $$F(u, v, w)F(u',v',w') = \frac{N^2}{\alpha^6\pi^3}e^{-\frac{c^2+c'^2}{\alpha^2}}$$

where $$c^2 = u^2 + v^2 + w^2 \text{ and } c'^2 = u'^2 + v'^2 + w'^2.$$

Calling $\frac{1}{\alpha} = \beta$ one has the above expression given by

$$\nu_a = \frac{N^2\beta^6}{\pi^3}e^{-\beta^2(c^2+c'^2)}\ \delta^2\ C_r \cos \theta\ dkdudvdwdu'dv'dw'.$$

For purposes of convenience in this deduction the previous δ will be replaced by σ.

If this number be multiplied by V, the volume, then one has all the α impacts in the volume V in the time τ given by

$$n_\alpha \tau = \frac{n^2\beta^6\tau}{V\pi^3} e^{-\beta^2(c^2+c'^2)}\sigma^2 C_r \cos\theta dk du dv dw du' dv' dw'.$$

Now $C_r \cos\theta$ is the same as the C_{r_n} used above. It is the normal component of relative velocity of the molecules. Thus to get the sum $\sum C_{r_n}$ for the α collisions only, one has but to multiply the number of collisions $n_\alpha \tau$ by $C_r \cos\theta$. Thus

$$\sum_\alpha C_{r_n} = \frac{n^2\beta^6\tau}{V\pi^3} e^{-\beta^2(c^2+c'^2)}\sigma^2 C_r^2 \cos^2\theta dk du dv dw du' dv' dw'.$$

To get the summation, one must integrate over dk, $dudvdw$ and $du'dv'dw'$. Since $dk = \sin\theta\, d\theta d\phi$, the integration over the $d\phi$ gives the factor 2π, and that over $d\theta$ (*i.e.*, of $\sin\theta\cos^2\theta d\theta$ from 0 to $\left(\frac{\pi}{2}\right)$ gives $\frac{1}{3}$, one has for all impacts between the molecules with the velocities uvw and $u'v'w'$ (*i.e.*, the A and B type molecules in the volume V (see Sec. 28)) the quantity

$$\sum_{AB} C_{r_n} = \frac{2\pi}{3}\frac{n^2\beta^6\tau\sigma^2}{\pi^3 V} e^{-\beta^2(c^2+c'^2)} C_r^2 du dv dw du' dv' dw'.$$

The integration over the $dudvdw$ and $du'dv'dw'$ requires a transformation of variables. Let

$$\frac{1}{2}(u + u') = U_1 \qquad u' - u = U_2$$
$$\frac{1}{2}(v + v') = V_1 \qquad v' - v = V_2$$
$$\frac{1}{2}(w + w') = W_1 \qquad w' - w = W_2$$

The quantities with the subscripts 1 are the components of velocity of the common center of gravity of the two molecules, and those with the subscript 2 are the components of the relative velocity C_r. The product $(dudu')(dvdv')(dwdw')$ must now be changed in terms of the new variables. From the above,

$$dU_1 = \frac{1}{2}du + \frac{1}{2}du'.$$
$$dU_2 = -du + du'.$$

Thus $dU_1 dU_2 = dudu'$ and similarly for the V and W components. Hence $\quad dudvdwdu'dv'dw' = dU_1 dV_1 dW_1 dU_2 dV_2 dW_2.$

Also $c^2 + c'^2 = u^2 + u'^2 + v^2 + v'^2 + w^2 + w'^2$

$$= 2(U_1^2 + V_1^2 + W_1^2) + \frac{1}{2}(U_2^2 + V_2^2 + W_2^2)$$

and $C_r = \sqrt{U_2^2 + V_2^2 + W_2^2}.$

Hence the expression

$$\frac{2\pi}{3}\frac{n^2\beta^6\tau\sigma^2}{\pi^3 V}e^{-\beta^2(c^2+c'^2)}C_r^2 dudvdwdu'dv'dw'$$

becomes

$$\frac{2\pi}{3}\frac{n^2\beta^6\tau\sigma^2}{\pi^3 V}e^{-\beta^2[2(U_1^2+V_1^2+W_1^2)+\frac{1}{2}(U_2^2+V_2^2+W_2^2)]}(U_2^2 + V_2^2 + W_2^2)dU_1dV_1dW_1dU_2dV_2dW_2.$$

Since in polar coordinates

$$U_1 = C\sin\theta\cos\phi \qquad U_2 = C_r\sin\theta'\cos\phi'$$
$$V_1 = C\sin\theta\sin\phi \qquad V_2 = C_r\sin\theta'\sin\phi'$$
$$W_1 = C\cos\theta \qquad W_2 = C_r\cos\theta'$$

and $dU_1dV_1dW_1dU_2dV_2dW_2$

$$= C^2dC\sin\theta d\theta d\phi C_r^2 dC_r\sin\theta' d\theta' d\phi'$$

therefore the equation becomes

$$\frac{2\pi}{3}\frac{n^2}{\pi^3}\frac{\beta^6\tau\sigma^2}{V}e^{-\beta^2(2C^2+\frac{1}{2}C_r^2)}C^2dC\sin\theta d\theta d\phi C_r^4 dC_r\sin\theta' d\theta' d\phi'.$$

Now C and C_r must be integrated from 0 to ∞, θ and θ' from 0 to π, ϕ and ϕ' from 0 to 2π, and finally the expression must be divided by 2, since the expression has been integrated over all A molecules and all B molecules, thus counting the impacts twice. Thus

$$\sum C_{r_n} = \frac{2\pi}{3}\frac{n^2}{V}\frac{\beta^6\tau\sigma^2}{2\pi^3}\int_0^\infty\int_0^\infty\int_0^\pi\int_0^{2\pi}\int_0^\pi\int_0^{2\pi}e^{-\beta^2[2C^2+\frac{1}{2}C_r^2]}$$
$$C^2C_r^4\sin\theta\sin\theta' dCdC_r d\theta d\theta' d\phi d\phi'.$$

Integration over ϕ and ϕ' gives $4\pi^2$, over θ and θ' gives the factor 4, whence

$$\sum C_{r_n} = \frac{16\pi^3 n^2\beta^6\tau\sigma^2}{3\pi^3 V}\int_0^\infty e^{-2\beta^2C^2}C^2dC\int_0^\infty e^{-\frac{\beta^2C_r^2}{2}}C_r^4dC_r,$$

which finally yields

$$\sum C_{r_n} = \frac{n^2\pi\sigma^2\tau}{\beta^2 V} = \frac{2}{3}\frac{n^2C^2\pi\sigma^2\tau}{V}.$$

This yields for R the repulsive virial, $R = \dfrac{-m\pi\sigma^3 n^2C^2}{3V}.$

Thus the virial must still be corrected by adding R to get the true equation of state, and one has

$$\left(p + \frac{a}{V^2}\right)V - \left(\frac{2}{3}\frac{\pi m\sigma^3 n^2 C^2}{3V}\right) = \frac{1}{3}nmC^2$$

or

$$\left(p + \frac{a}{V^2}\right)V = \frac{1}{3}nmC^2\left\{1 + \frac{2}{3}\frac{\pi\sigma^3 n}{V}\right\}.$$

Now $\frac{2}{3}\pi\frac{\sigma^3 n}{V}$ is $4\left(\frac{4}{3}\pi r^3\frac{n}{V}\right)$ or 4ω, where ω is the volume of all the spherical molecules in unit volume. This quantity was called b in the previous deduction of Van der Waals' equation. Thus one can write

$$\left(p + \frac{a}{V^2}\right)V = \frac{1}{3}nmC^2\left(1 + \frac{b}{V}\right)$$

To a first approximation this goes over into the form

$$\left(p + \frac{a}{V^2}\right)V\left(1 - \frac{b}{V}\right) = \frac{1}{3}nmC^2,$$

and hence

$$\left(p + \frac{a}{V^2}\right)(V - b) = \frac{1}{3}nmC^2.$$

This is the Van der Waals' equation deduced in a much simpler fashion in Sec. 48. This deduction is, however, more rigorous, and it does show quite definitely what type of forces are involved and what assumptions must be made. The essential assumption concerning the $\phi(r)$ was that it was active over such short distances that it made no difference whether the limits of integration for r were over the dimensions of the vessel or to infinity. The simple derivation also contained the assumption that the vessel was several times larger than the radius of the sphere of action. The value of the force function thus still remains undetermined and it depends both on the magnitude of the force constant and on the variation with r to determine whether it will obey the conditions imposed. The small size of the correction terms and the agreement of the equation indicate that it is fulfilled. This deduction also gives the proper justification for taking $b = 4\omega$, which was discussed in Sec. 49.

51. Determination of a and b from Measurements on the Expansion Coefficients of a Gas. Evaluation of the Absolute 0 of Temperature. Since the deviations of the true gases from the behavior of an ideal gas are caused, to a first approximation, by the constants introduced into the more correct Van der Waals' equation, a study of these deviations should make it possible to

evaluate these constants. Experimentally, the deviations appear in the behavior of gases with change in temperature. If the volume and pressure changes with temperature are evaluated experimentally, comparison with the coefficients for the ideal gas will permit the values of a and b to be determined from the relations to be deduced. Incidentally, it will be found essential to evaluate α, the coefficient of expansion for an ideal gas. The value of this quantity α leads at once to the establishment of the experimental value for the absolute zero of temperature in terms of the Centigrade scale.

In proceeding to the deduction, it is well to recall the definition of the coefficient of expansion for an ideal gas. As was shown in Sec. 1, the equation for an ideal gas $pv = RT$ follows at once from the experimental relation giving the volume or pressure change of an ideal gas with temperature which reads

$$v = v_0(1 + \alpha t)$$

or

$$p = p_0(1 + \alpha t).$$

Since the ideal gas has forceless molecules and the molecules have no volume, α is the same in both cases and both p and v vanish when $t = -\frac{1}{\alpha}$.

In the present case (*i.e.*, that of a real gas), however, the gas does not have the properties of the ideal gas, and its equation of state is expressed by

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT.*$$

Since RT was derived from the value of α for an ideal gas, RT is $\alpha p_o v_o\left(\frac{1}{\alpha} + t\right)$, where α is the expansion coefficient for the ideal gas. Since $p_o v_o$ on the kinetic theory is $\frac{1}{3}nmC_o{}^2$, the RT may be replaced by the expression $\frac{1}{3}nmC_o{}^2(1 + \alpha t)$. For the sake of simplicity in this deduction the value of C at 0°, which is denoted as C_o, will be written merely C. Hence the equation of state (for a real gas) for the present purpose takes the form given by the equation

$$\left(p + \frac{a}{v^2}\right)(v - b) = \frac{1}{3}nmC^2(1 + \alpha t).$$

* For convenience from now on the volume of the gas V will be represented by v.

Now for a real gas the volume and pressure at 0° abs. will not be 0, for the molecular volumes and intermolecular forces exist at 0° abs. Thus the coefficient α will no longer typify the *volume or pressure coefficient* of expansion of a real gas.

The *pressure coefficient* of expansion is defined as $\beta = \dfrac{p_t - p_o}{tp_o}$, that is, the pressure at $t°$ less the pressure at 0° divided by t times the pressure at 0°. It is the rate of change of pressure with temperature divided by the initial pressure. To obtain this for a real gas, p_t and p_o must be introduced from Van der Waals' equation:

$$\left(p_t + \frac{a}{v^2}\right)(v - b) = \frac{1}{3}nmC'^2(1 + \alpha t),$$

$$\left(p_o + \frac{a}{v^2}\right)(v - b) = \frac{1}{3}nmC'^2(1 + 0 \times \alpha).$$

Subtracting to get $p_t - p_o$, one obtains

$$(p_t - p_o)(v - b) = t\alpha\left(\frac{1}{3}nmC'^2\right).$$

Hence $\beta = \dfrac{p_t - p_o}{tp_o}$ is given by $\beta = \dfrac{\alpha}{p_o}\dfrac{1}{3}\dfrac{nmC'^2}{v - b}$, but $\left(p_o + \dfrac{a}{v^2}\right) = \dfrac{1}{3}\dfrac{nmC'^2}{v - b}$ and therefore

$$\beta = \frac{\alpha}{p_o}\left(p_o + \frac{a}{v^2}\right) \qquad \text{or} \qquad \beta = \alpha\left(1 + \frac{a}{v^2 p_o}\right).$$

If α were known, then, since β is measured experimentally, knowing v and p_o, a could be determined for the gas.

Hence this equation can be of some use if α is known. To get further information, the *volume* coefficient of expansion must be evaluated in terms of Van der Waals' equation.

The *volume coefficient* of expansion for a gas is defined as

$$\alpha_v = \frac{v_t - v_o}{tv_o}.$$

Thus in analogy to the case for the pressure coefficient,

$$\left(p + \frac{a}{v_o^2}\right)(v_o - b) = \frac{1}{3}nmC'^2(1 + \alpha \times 0)$$

$$\left(p + \frac{a}{v_t^2}\right)(v_t - b) = \frac{1}{3}nmC'^2(1 + \alpha t)$$

$$p(v_t - v_o) + a\left(\frac{1}{v_t} - \frac{1}{v_o}\right) - ab\left(\frac{1}{v_t^2} - \frac{1}{v_o^2}\right) = \left(p + \frac{a}{v_o^2}\right)(v - b)\alpha t$$

and $v_t - v_o = \alpha_v v_o t$,

therefore

$$(v_t - v_o)\left(p - a\frac{1}{v_t v_o}\right) + \frac{v_t^2 - v_o^2}{v_o^2 v_t^2}ab = \left(p + \frac{a}{v_o^2}\right)(v_o - b)\alpha t$$

$$p\alpha_v v_o t - \frac{a\alpha_v t}{v_t} + \frac{\alpha_v abt v_o(v_t - v_o)}{v_o^2 v_t^2} = \left(p + \frac{a}{v_o^2}\right)(v_o - b)\alpha t;$$

dividing by $v_o t$,

$$\alpha_v\left[p - \left(\frac{a}{v_t v_o}\right)\left(1 - \frac{b(v_o + v_t)}{v_o v_t}\right)\right] = \left(p + \frac{a}{v_o^2}\right)\left(1 - \frac{b}{v_o}\right)\alpha$$

and therefore

$$\alpha_v = \alpha\frac{\left(p + \frac{a}{v_o^2}\right)\left(1 - \frac{b}{v_o}\right)}{p - \left(\frac{a}{v_t v_o}\right)\left(1 - b\frac{v_t + v_o}{v_o v_t}\right)}.$$

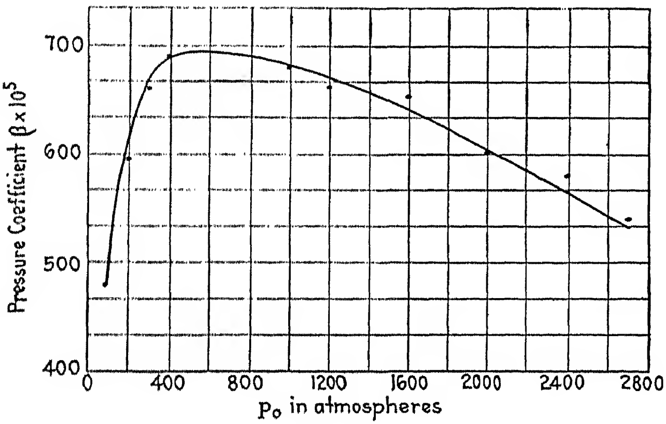

FIG. 28.

Thus α_v is a much more complicated function of α, a, and b than was β. It is seen, however, that if the constant α for an ideal gas can be evaluated for certain gases, and if, from the expression for β, a can be found for gases other than those used in getting α, then b can be found from α_v.

These two expressions for α_v and β in terms of a, b, and α merit some discussion.

First the expression leads to one result which has been verified experimentally and is hence interesting.

$$\beta = \alpha\left(1 + \frac{a}{v^2 p_o}\right).$$

Thus β plotted as a function of p_o should vary in the following fashion: α is a constant, a is also a constant, while $p_o v$ is nearly con-

stant for some pressures. Hence over the range where pv is constant, and since as p_0 increases, the remaining term in p_0v^2 decreases, therefore β should start from a given value and increase. At the point where the volume becomes so small that, owing to the size of the molecules, v does not decrease as fast as p increases, *i.e.*, where p_0v^2 starts to increase, then β should begin to decrease. Thus a curve for β as a function of p_0 of the form shown in Fig. 28 should be obtained. The curve shown is actually one found experimentally for oxygen gas.

Again writing the expressions for α_v and β, the following cases may be discussed:

$$\beta = \alpha\left(1 + \frac{a}{v^2p_0}\right).$$

$$\alpha_v = \alpha\frac{\left(p + \frac{a}{v_0^2}\right)\left(1 - \frac{b}{v_0}\right)}{\left(p - \frac{a}{v_1v_0}\right)\left(1 - b\frac{v_1 + v_0}{v_1v_0}\right)}$$

Case I. If $a = 0 = b$.

The gas is ideal; $\beta = \alpha$ and $\alpha_v = \alpha$.

Case II. If $a = 0$, $b > 0$.

Then $\beta = \alpha$ and $\alpha_v = \alpha\left(1 - \frac{b}{v_0}\right)$.

Thus α is greater than α_v. If α is obtained from β, and if α_v is measured, b may be evaluated. This case is nearly fulfilled by the gases He and H_2.

Case III. If $a > 0$, $b = 0$.

Then
$$\beta = \alpha\left(1 + \frac{a}{v_0^2p_0}\right).$$

$$\alpha_v = \alpha\frac{\left(p + \frac{a}{v_0^2}\right)}{p - \frac{a}{v_1v_0}}.$$

or
$$\alpha = \alpha_v\left(1 + \frac{a}{v_0^2p} + \frac{a}{pv_1v_0}\right).$$

Whence $\alpha_v > \beta > \alpha$. Such a case might be covered by a condensible gas.

Case IV.—If, as is really the case for H_2 and He, $b > a > 0$,

then
$$\beta = \alpha\left(1 + \frac{a}{v_0^2p_0}\right)$$

and $$\alpha_v = \alpha\left[\left(1 - \frac{b}{v_o}\right) + \left(1 - \frac{b}{v_o}\right)\frac{a}{v_o{}^2p} + \cdot\ \cdot\ \cdot\ \right],$$

whence $\beta > \alpha$ and $\alpha > \alpha_v$ for $1 - \dfrac{b}{v_o} < 1$.

Therefore for the gases He and H_2

$$\beta > \alpha > \alpha_v.$$

The inequality in Case IV serves as a means of evaluating α practically. For H_2, α_v and β have been measured. Thus for H_2 the accurate older values for these constants found are $\beta = 0.003662$ and $\alpha_v = 0.003660$. α was taken, with a fair degree of certainty, to be 0.003661. This value of α gives a value for the absolute zero on the Centigrade scale of $-273.15°C$ The present value is given as $-273.13°C$. from other data.

Thus having α, a and b can be obtained. As a matter of fact, it is possible to get a and b much more accurately from other data, for the differences in α_v and β are small, and these small differences are very important in evaluating a and b. As a and b can be determined very much more accurately by methods to be discussed later, these more accurate values are at the present time inserted into the equations above and thus serve to evaluate α. Thus an accurate value of α is obtained and hence the value of T may be accurately determined. T is, however, also more accurately determined today by the Joule-Thomson effect on thermodynamic reasoning.

It also happens that both α_v and β vary with temperature in some gases. Since these equations show how α_v and β depend on a and b, the variation of a and b with temperature may be investigated. Actually, these quantities were assumed to be constants independent of p, v, and T in deducing Van der Waals' equation. A study of the variation of α_v and β with temperature indicates that neither of these is constant with temperature for all gases. These deviations and their significance can be much more profitably discussed in connection with other work, and it will be seen that the variations of a and b with conditions lead to a still more profound understanding of the nature of molecular collisions and structure.

52. The Graphical Representation of the Equation of State and the Evaluation of a and b from Critical Data.—In the preceding section Van der Waals' equation was used to determine the absolute zero of temperature. In using it no attempt was made

to plot it or to determine the form of the equation. Since it represents the behavior of the gases, it is best to analyze it graphically. It is seen at once that the equation

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

is an equation in three independent variables, p, v, and T, having two constants whose relative and absolute values vary from gas to gas. To plot it for a given set of values of a and b would not give the general view of it required, particularly if a and b are not known. With the use of the calculus, a very good general idea of its shape and its significance can be obtained.

To simplify the discussion, T could be considered a constant and the attention concentrated on the relation between p and v. Then to gain a more perfect picture, this could be done for a whole series of different values of T. The curves plotted with p as ordinates and v as abscissæ, holding T a constant, are called *isothermal curves*, or *isotherms*, the term coming from the Greek *iso*, meaning equal, and *thermos* meaning temperature. They are curves of equal temperature. It is seen at once that the Van der Waals' equation regarded in this way and multiplied out has the form

$$v^3p - v^2(RT + pb) + av - ab = 0.$$

It is thus a cubic equation in v. Such an equation is known from elementary algebra to have either three real roots or only one real and two imaginary roots, depending on the values of the constants—that is to say, for one value of p there will be either three real values of v or only one real value. The conditions determining these will be found later.

The Van der Waals' equation may be written in the form

$$p = \frac{RT}{v - b} - \frac{a}{v^2}.$$

It is seen from this that for values of v near b the pressure p approaches infinity. For values of v smaller than b the equation has no physical meaning, as p is then negative. Furthermore, if v becomes very large p becomes vanishingly small. Thus the two extremes of the curves are definitely determined, for as v approaches b, p becomes infinite and as v approaches infinity p approaches zero asymptotically. In the extremes the curve descends in p as v increases, approaching zero in the limit. It is therefore part of the way concave upward. In between, it may

have maxima and minima, and, in fact, the three roots lead one to expect, under some conditions, a complex course.

The maxima and the minima are found by setting the first derivative equal to zero, and solving the equation; that is, in finding the points were $\frac{dp}{dv}$ is zero.

$$\frac{dp}{dv} = \frac{-RT}{(v - b)^2} + \frac{2a}{v^3}.$$

In the expression above, $\frac{dp}{dv}$ is negative for values of v that are very small, for near b the term $RT/(v - b)^2$ can become greater than the $\frac{2a}{v^2}$ term. Again, $\frac{dp}{dv}$ is negative for very large values of v, for in this case, since v^3 increases more rapidly than v^2, the second term becomes less than the first. Thus for large and small values of v the first derivative is negative, meaning that the curve slopes towards increasing v. Between large and small values of v the $\frac{dp}{dv}$ term is positive under some conditions and hence the curve slopes to the decreasing v's.

The values of v for maxima and minima are given by solving the equation above when $\frac{dp}{dv} = 0$. This solution yields an equation in a, b, v, and T of the form

$$T = \frac{2a(v - b)^2}{Rv^3}.$$

This is a cubic in v and thus has three real roots or one real and two imaginary roots. That is, there are either three values of v which satisfy this equation for maxima or minima, or there is only one. Thus two conditions exist for the curves, that is, they have either three points where $\frac{dp}{dv} = 0$ or only one. Now the course of the equation which was deduced from the value of the sign of $\frac{dp}{dv}$ for values between $v = b$ and $v = \infty$ indicates that the curve descends with increasing v to a minimum, rises when $\frac{dp}{dv}$ is positive to a maximum, and finally descends asymptotically to 0 at $v = \infty$. There appear to be between $v = b$

and $v = \infty$ then, only one maximum and one minimum. The three roots of the equation for maxima and minima indicate, however, three points at which $\frac{dp}{dv} = 0$.

Thus one of the three points must lie at values of v less than b. It is therefore of no importance for the present analysis. That the third root lies in this region can be shown by transforming the equation for maxima and minima to one whose origin is not at 0 but at b. If this is done the expression becomes $RT(b + w)^3 - 2aw^2 = 0$, where $w = v - b$. This equation expanded gives

$$w^3 + \left(3b - \frac{2a}{RT}\right)w^2 + 3b^2w + b^3 = 0.$$

Now a well-known relation in the theory of equations says that for a cubic the product of the three roots must be equal to the negative value of the last term, that is, that the three roots w_1, w_2, and w_3 multiplied together should be equal to $-b^3$. But in the equation above the last term is positive and hence one of the three roots must be negative. In such an equation for the case that two of the roots are imaginary and one only is real the relation further indicates that the real root is negative. Hence referred to b as origin, one of the three points at which $\frac{dp}{dv}$ is 0 must always lie at negative values, that is, one of the three maxima (or when there is only one real maximum or minimum that one) must lie at values of v smaller than b. This agrees with the conclusions arrived at from the slopes, namely, that the isotherm has either no maximum or minimum or only two. The shape of the isotherms must therefore take the form either of the curve marked 13.1° or 100.1° in Fig. 29 for the cases where there are three real roots and one real root respectively. It is seen that this curve also fulfils the condition for three real roots of Van der Waals' original equation, for a given value of p will intersect the curve in three places. To find the values for the maxima and minima, numerical values for a, b, and T would be required. By evaluating $\frac{d^2p}{dv^2}$ for these points, one would find, from the sign of $\frac{d^2p}{dv^2}$, to which value of v the maximum belonged. Letting $\frac{d^2p}{dv^2}$ equal zero would determine the position of the point of inflection between the maximum and minimum.

Now the expression for the maxima and minima,

$$T = \frac{2a(v - b)^2}{Rv^3},$$

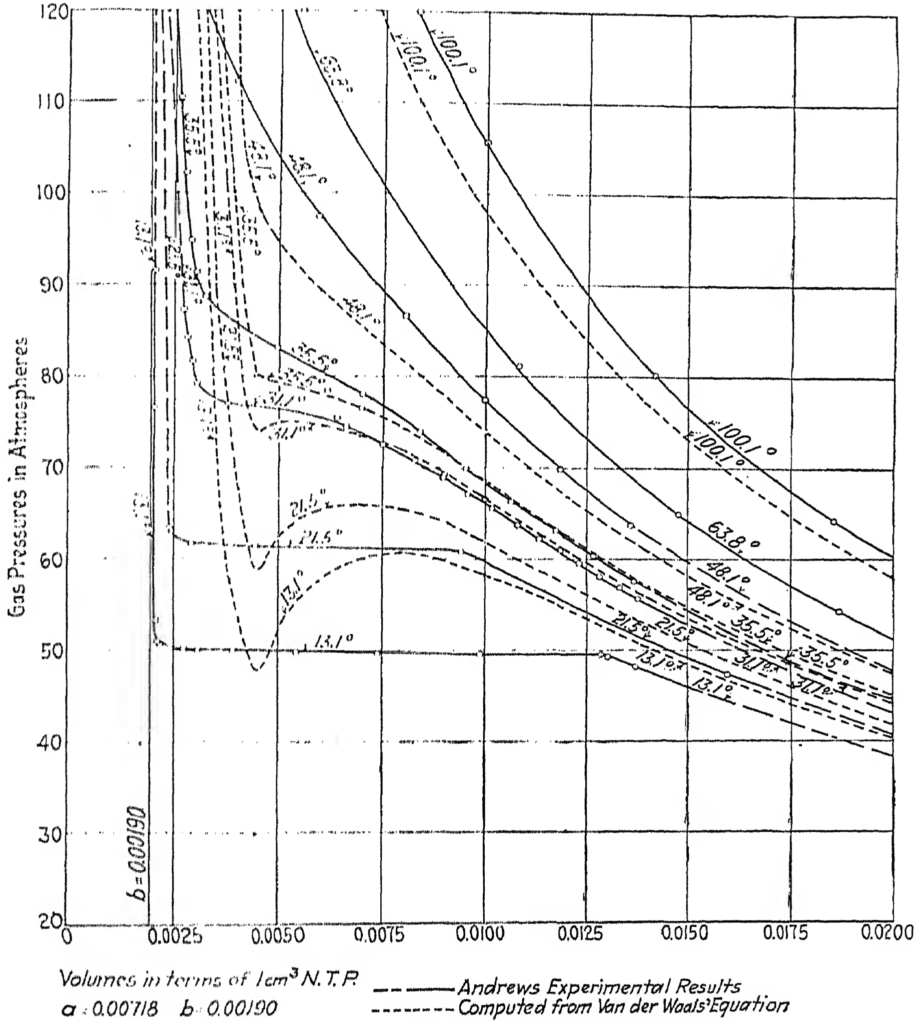

FIG. 29.

is a continuous function of v. For values of v small enough to approach b it has a small value, and for values of v which are very great, since v^3 increases more rapidly than $(v - b)^2$, it has small values. Between the two extremes it has a maximum

value. Physically, there exist values of T above this maximum which must lie above this curve, that is, there are conditions of temperature in which the three maxima and minima do not exist. At such temperatures, however, the isotherms still exist, but they can have only the one minimum; and this one has values of v less than b. In such curves the sign of $\frac{dp}{dv}$ is always negative, T being so large that $\frac{2a}{v^3}$ can never exceed $\frac{RT}{(v-b)^2}$. The curve then slopes down continually to higher values of v. The particular temperature at which the curve ceases to have one minimum and one maximum above $v = b$ can be called the *critical* temperature. The value of T, when the function is a maximum is found by setting $\frac{dT}{dv}$ equal to zero and solving for v.

$$\frac{dT}{dv} = \frac{-6aRv^2(v-b)^2 + 2aRv^3(2v-2b)}{3Rv^4} = 0$$

$$-3(v-b)^2 + 2v^2 - 2vb = 0$$

$$v^2 - 4bv + 3b^2 = 0$$

$$(v-3b)(v-b) = 0$$

$$v_c = 3b$$

or

$$v_c = b.$$

For $v_c = b$, T is zero and this is a minimum. Thus the maximum is at $v_c = 3b$.

Accordingly, T_c can be found at once to be

$$T_c = \frac{2a(3b-b)^2}{R(3b)^3} = \frac{8ab^2}{27Rb^3} = \frac{8a}{27Rb}.$$

Thus there is a value of T depending on the ratio between a and b for which the curves pass into curves having no point of inflection.

Thus if a family of isotherms were plotted for the Van der Waals' equation at different values of T, it would be found that above the value T_c the curves were simple curves dropping down to 0 at great values of v with no points of inflection as in the curve for 100.1° and 48.1° (Fig. 29). Below this value of T the curves have a minimum, a maximum, and a point of inflection. At the temperature T_c the curve passing through it has the maximum, minimum, and point of inflection lying infinitely close together. Hence this condition should make it possible to find a series of relations between p_c, v_c, and T_c and the con-

stants a and b at this point. To find these, merely three equations need be used:

$$p = \frac{RT}{(v - b)} - \frac{a}{v^2}, \tag{1}$$

the original equation.

$$\frac{dp}{dv} = -\frac{RT}{(v - b)^2} + \frac{2a}{v^3} = 0, \tag{2}$$

the expression for the maximum and minimum which now lie at the same point.

$$\frac{d^2p}{dv^2} = \frac{2RT}{(v - b)^3} - \frac{6a}{v^4} = 0, \tag{3}$$

the expression for the point of inflection.

Since maximum, minimum, and point of inflection lie together Eqs. (2) and (3) may be written in the forms

$$RT_c = \frac{2a}{v_c^3}(v_c - b)^2$$

$$RT_c = \frac{3a}{v_c^4}(v_c - b)^3,$$

where T_c and v_c now correspond to the same isotherm, the critical one. For this isotherm Eqs. (2) and (3) can be combined, since $RT_c = RT_c$.

Therefore $$2a = \frac{3a(v_c - b)}{v_c}.$$

Therefore $v_c = 3b$.

This was found before as the condition for a maximum T_c for which three maxima or minima ceased to exist. From Eq. (2) and the value for v_c above,

$$\frac{dp}{dv} = \frac{-RT_c}{4b^2} + \frac{2a}{27b^3} = 0.$$

Therefore $T_c = \dfrac{8a}{27Rb}$.

Finally, from T_c and v_c one has $p_c = \dfrac{8a}{54b^2} - \dfrac{a}{9b^2} = \dfrac{a}{27b^2}$.

Thus one has a set of three equations between T_c, v_c, and p_c and a and b.

$$v_c = 3b,\ T_c = \frac{8a}{27Rb},\ \text{and}\ p_c = \frac{a}{27b^2}$$

and if T_c, v_c, and p_c can be measured one ought to get a and b.

Now the question arises, Do real gases follow these laws? If this is so, it should be possible to evaluate a and b either from the isotherms or from values of p_c, T_c, and v_c taken from observations.

Van der Waals, who as a mature man left business to undertake scientific study, deduced his now famous equation in his doctor's dissertation at Leyden in 1873. Attempts at bettering the ideal gas equation had first been made by Clausius (see Sec. 18), who introduced the correction for the volume of the molecules into the equation by writing $v - b$ in place of v, and by Hirn, who in 1864 added an expression to the pressure term to take account of the attraction of the molecules. This term, however, did not give the variation of the force with the volume. It was by a consideration of Laplace's theory of surface tension that Van der Waals supplied the missing relation and completed the theory. About ten years previous to this Andrews studied a peculiar phenomenon first observed by Cagniard de la Tour. This was that if a tube containing liquid carbon dioxide were heated gradually, a temperature was reached (31.1°C) at which the meniscus dividing the liquid and gaseous phases disappeared. Investigation showed that no matter what the pressure became above this temperature the CO_2 which had been partly in the gaseous, partly in the liquid phase below this point changed to a homogeneous, transparent state in which there was no indication of the gas and liquid. The temperature at which this occurred was called the critical temperature. This curious observation directed attention to the behavior of gases in general at the higher pressures, and other gases like SO_2 were found which showed this behavior near ordinary temperatures. Today, this temperature has been determined for most of the well-known gases and vapors. Andrews began a series of measurements extending from 1863 to 1876, in which he studied the behavior of the isotherms of CO_2 at various temperatures and up to pressures of 200 atmospheres. These data gave Van der Waals the material upon which to test his theory.

Van der Waals first used the accurate measurements of Regnault on the isotherms of CO_2 which were carried to pressures of 27 atmospheres. Solving for a and b, using the methods depending on the pressure and volume coefficients, he estimated a to be .00874 atmosphere cm^6, and b to be 0.00023 cm^3. Introducing these values into his equation, he was able to obtain a closer agreement between his curve and Regnault's experimental points than Regnault obtained with his empirical equation. He then applied this equation to the computations in the region of Andrews' measurements. In this case the agreement was not so striking. In fact, the comparison of the computed curves and

the observed curves of Andrews are not given in texts because of the discouraging nature of the agreement. It seems, however, that the direct comparison is of sufficient value in indicating the strength and the deficiencies of the theory to merit reproduction.

To compute the isotherms it is best to use the values of a and b given by the critical data obtained by Andrews, since these are more accurate than the values deduced from Regnault's curves. Using these values, it is then equivalent to fitting the system of theoretical isotherms to *one point*, the *critical point*, on the observed system of isotherms. Andrews obtained for CO_2 the following values: $T_c = 31.1°C.$, $p_c = 73$ atmospheres, and $v_c = 0.0066$ cm³ for a cm³ of gas at N.T.P. Before using these one might compare these values with those computed by Van der Waals from the equation using the a and b taken from Regnault's data, namely, $a = 0.00874$ and $b = 0.0023$.

$v_c = 3b$, $v_c = 3(0.0023) = 0.0069$ cm³ *computed,* 0.0066 cm³ *observed.*

$$T_c = \frac{8a}{27bR} \qquad R = \frac{1}{273} \qquad T_c = \frac{8(0.00874)}{27(0.0023)\frac{1}{273}} = 307° \text{ abs.}$$

$T_c = 34°C.$ *computed;* 31.1°C. *observed.*

$$p_c = \frac{a}{27b^2} = \frac{0.00874}{27(0.0023)^2} = 61$$ *atmospheres computed;* 73 *atmospheres observed.*

For the computations of a and b from Andrews' results it is best to use the equations, $T_c = \frac{8a}{27bR}$ and $p_c = \frac{a}{27b^2}$, since v_c was difficult to obtain with certainty from the measurements, while p_c and T_c could be accurately measured. These give $a = \frac{27R^2T_c^2}{64(p_c)}$ $= 0.00717$ atmosphere $\times$ cm⁶ and $b = \frac{RT_c}{8p_c} = 0.00191$ cm³. As a partial check on these values, b can be compared with the observed $v_c = 0.0066$. Since $v_c = 3b$, the data give 0.00573. Thus there is some discrepancy between the values which may be attributed to errors in measuring b as well as errors in the theory of the equation to be discussed later.

With the aid of these constants, the isotherms may be computed from Van der Waals' theory as follows, taking 0.00718 for a and 0.00190 for b:

$$\left(p + \frac{0.00718}{v^2}\right)(v - 0.0019) = RT.$$

Now if the gas were ideal (*i.e.*, a and b were 0) and p were expressed in atmospheres while v was taken as 1 cm³, pv would be unity. Thus RT would be unity. At 0°C. and 760 mm pressure R would be $1/273$ for this gas. Thus for the ideal gas $pv = \frac{T}{273}$. For the real gas with a and b finite, however, at 0°C. and 1 atmosphere the true p and the true v are given by the above. Hence, the above equation for 1 atmosphere and 1 cm³ becomes

$$(1 + 0.00718)(1 - 0.0019) = 1.0053.$$

Therefore, in order to compute p and v the equation becomes

$$\left(p + \frac{0.00718}{v^2}\right)(v - 0.0019) = 1.0053\frac{T}{273}.$$

Hence, by putting in the values of T, the absolute temperature, and introducing values of v, the equation may be solved for p. Taking the values of T and v corresponding to Andrews' experimental isotherms for 13.1, 21.5, 31.1, 35.5, 48.1, and 100.1°, the Van der Waals' isotherms were computed from the above equation. The resulting dashed curves may be seen in comparison to Andrews' actual curves in full lines in Fig. 29.

It is observed at once that in this region the close agreement that Van der Waals found for Regnault's results does not exist between the observed and computed values. It is, however, seen that, leaving a certain feature of the low temperature isotherms aside (*i.e.*, the maximum and minimum), the general shape of the curves and the evolution of their form with temperature are strikingly similar. The nature of the similarities indicates that qualitatively the phenomenon is represented by the Van der Waals' equation. The cause for the agreement of Regnault's values together with the apparent failure here can be easily seen by looking at the equation as used for computation.

$$p = \frac{1.0053\left(\frac{T}{273}\right)}{(v - 0.0019)} - \frac{0.00718}{v^2}.$$

It is seen that p is given by the *difference* of two terms. These terms for small values of v are especially large and a small change in a or b will make an enormous change in p. Thus unless a and b were closely constant and known to several significant figures an accurate superposition of the curves in this region would be impossible. When v, however, is larger, say near 1 or 2 atmos-

pheres, the corrections a and b become insignificant. Errors in their values are negligible and a close agreement is to be expected. Van der Waals, who was interested in establishing his theory, did not publish curves of this sort. Instead, he assumed the value of a taken from Regnault's values. Then, taking p and v from Andrews' results, he computed the value of b. The values found for b varied between 0.0025 and 0.0015 in extreme cases, while they lay close to the value 0.0023 from Regnault's work, when data taken for v greater than 0.004 cm³ were used. Now it can be seen from Secs. 19 and 49 on the value of Van der Waals' b that if v is less than $2b$, the spheres of exclusion of all the molecules must interpenetrate. Thus, on a collision, the average distance of approach of molecules is decreased and the shortening of the free path is changed. This change is of such a nature that b is no longer 4ω, but less. Hence, the rapid decrease of b with values of v below 0.004 cm³ is a direct consequence of the kinetic theory and was to be expected. Thus Van der Waals' initial assumption that b was constant independent of v was not quite correct in the extreme case of Andrews' measurements. Neglecting this deviation, it can be seen that the values of b computed by Van der Waals from Andrews' results show a fair constancy, and the sensitiveness of the plotted curves to these small deviations is demonstrated.

Before going on to discuss more in detail the causes for deviation, the apparently most glaring discrepancy must be discussed. The experimental curves of Andrews below the critical temperature do not show the maxima and minima exhibited by Van der Waals' equation. Below the critical temperature the flat portions of Andrews' curves mark the point at which visible condensation was taking place. In the theoretical equation this discontinuity does not occur. In looking at the physical significance of the region lying between the maximum and the minimum of the theoretical curve, it is seen that it represents a region where with decreasing volume the pressure is falling. Thus the maximum is a region of unstable equilibrium, for as soon as it is reached the volume decreases of its own accord, since the pressure is not needed to maintain the small volume. It is not surprising that this region cannot be studied experimentally. Neither can the other regions near the maximum and the minimum be studied because of the instability of the gas in contact with its environment. In this case, however, it is the adhesive forces of the walls

which act to cause condensation of the liquid on them before the maximum is reached. Actually, in certain cases where great care is used in reaching the condition the curves can be followed beyond the straight linear portions observed by Andrews, that is, in certain cases, with supersaturated vapors and supercooled gases condensation is avoided temporarily. These represent points along the isotherms reaching into the region discussed but not to the maximum or minimum. This state is, however, so unstable that sudden mechanical shocks, particles of dust, or any slight disturbances cause almost explosive condensation. It is obvious that it is impossible to carry on accurate measurements in this region. Thus the failure to find the maxima and the minima of the theory is not a weakness of the theory but lies in technical difficulties involved in making measurements where external agencies such as the walls do not intervene. Above the critical temperature, of course, this difference disappears. No liquid can exist there and the theoretical and observed isotherms could be made to agree with remarkable precision by properly evaluating a and b for these conditions.

The serious deviations of the theory, as was pointed out, lie in assumptions as to the constancy of a and b. It was shown that in the most interesting region, that is, for v approaching b, b should not be a constant. There are other reasons why b should not be a constant. b depends on the radii of the assumed incompressible spherical molecules. Now, actually, it is known that molecules are not rigid spheres. They are complex planetary systems of negative electrical charges revolving about a positively charged central nucleus or sun, whose mass comprises most of the mass of the molecules. The repulsive forces in the atoms and molecules must be due to the repulsions of the outer negative charges of the electrons when the atoms approach each other sufficiently closely.[10] Thus the repulsions are due to the interactions of the force fields of the electrons at the surfaces of the molecules. These become appreciable when the distances between the outer electrons of two colliding molecules become less than the distances between the electrons and the nuclei of their respective atoms. The distance to which the molecules must approach each other before their kinetic energy of approach equals the potential energy of the repulsive forces and they consequently reverse their relative velocities and separate, having collided, is a function of their relative kinetic energies. Thus

the faster the molecules move, the closer they must approach in collisions. It is, therefore, not strange that σ and hence b, which is proportional to σ^3, should be a function of the temperature of the gas. Accordingly, the assumption of a constant b needs modification for changes in the volume and in the temperature of the gas.*

Again a was assumed a constant. Actually, as is seen from the deduction of the equation from the theorem of the virial in Sec. 50, this depends on the radius of the sphere of action of the forces between molecules, being small compared to the cube root of the volume. Otherwise the quantity could not be integrated from zero to infinity, and a would not be independent of v. Whether this holds at values of v which are close to $2b$ may well be doubted. In his book, "A System of Physical Chemistry," W. McC. Lewis determines the value of $\phi(r)$ (see Sec. 50) such that for all volumes a will be independent of v. It is argued that if a is to be a constant then the internal pressure must vary as $\frac{1}{v^2}$. If the law of force gives the force as $f = \frac{A}{r^x}$, the pressure p' will be propor-

* An interesting comparison is made by Jellinek[9] in his "Physical Chemistry," vol. 1, Part 1, p. 391. He shows that each of the isotherms of Andrews can be closely fitted (except in the unstable region) by Van der Waals' equation if the proper constants are chosen. Good agreements can be obtained at the following temperatures for the values of a and b given:

Temperatures	$b = 0.0023$, curves fit for a	$a = 0.008497$ curves fit for b
6.5°C.	0.008497	0.0023
64.0°C.	0.007529	
100.0°C.	0.006798	0.0032

Thus the equation fits for either b constant and a varied, or a constant and b varied. From 6.5 to 100° the a values vary 20 per cent when b is constant, and for a constant the b values may vary by 30 to 40 per cent in this same range. Jellinek says that the use of a variable a seems more adequate for this reason as well as from the indications of the data on the variation of β, the pressure coefficient, with temperature. On the other hand, Van der Waals' theory demands that b vary with the volumes when these become small and a might be expected to vary with volume also. So that variations in both a and b with volume and temperature are to be expected, a varying less with volume than b and b less with temperature than a.

tional to $\frac{f}{r^2}$, or $\frac{A}{r^{x+2}}$, since the area of the surface is proportional to r^2 and $v \propto r^3$. But from Van der Waals' equation $p' \propto \frac{1}{v^2}$ and v is the volume containing a given number of molecules. Since the distance between every two molecules, on the average, must be $\sqrt[3]{\frac{v}{n}}$ accordingly $r^3 \propto v$ and hence $p' \propto \frac{1}{r^6}$. Thus he claims that, since $\frac{1}{r^{x+2}} = \frac{1}{r^6}$, x must equal 4, that is $\varphi(r) \propto \frac{1}{r^4}$. This assumption applies to the case where the integration of the virial is carried out over the whole volume, and the forces extend over it all. If this rigid statement as to the law of force were correct, it would be only for this one special law of force that any approximation to a constant value of a with volume could be expected. Thus a in the extreme ranges of Andrews' values may be a function of v, though probably distinctly less so than b. Finally, the attractive forces causing the term a are the molecular forces of attraction which enter into cohesion. They are due to the interaction of the force fields produced by the combinations of positive and negative charges in the molecules.

The forces could then be regarded as due to the stray electrical lines of force from the charges present which do not succeed in completely neutralizing each other at small distances from the molecules. How such forces arise may be imagined from the cases of polar molecules, like those of HCl, in which the negative charges are segregated in different portions of the molecule. In HCl the Cl atom appears to have a preponderance of the negative charges and the H a preponderance of the positive charges. If two such polar molecules are near each other they will tend to orient themselves in their mutual fields so as to attract each other, *i.e.*, positive ends to negative ends. The law of force in such cases, however, falls off rapidly with the distance. Other molecules can be considered as being electrical quadripoles and even more complex configurations. A study of the work of Debye (see Secs. 95 to 97, Chap. X) and others on dielectric constants and their variation with temperature, as well as on conduction by electrolytes, will give some notion of the nature of the forces involved. If the temperature is so low that the potential energies of these molecules when in contact exceed their kinetic energies the molecules will "stick" on impact. That is

to say, the gas will condense. If not, there will be a resultant pressure measured by $\frac{a}{v^2}$ in Van der Waals' equation. The higher the temperature the greater the disorienting action on the molecules and the less chance there will be for the forces to act. The result will be that a is a function of the temperature just as the dielectric constant of gases is, and in this case would be expected to decrease as the temperature increases.

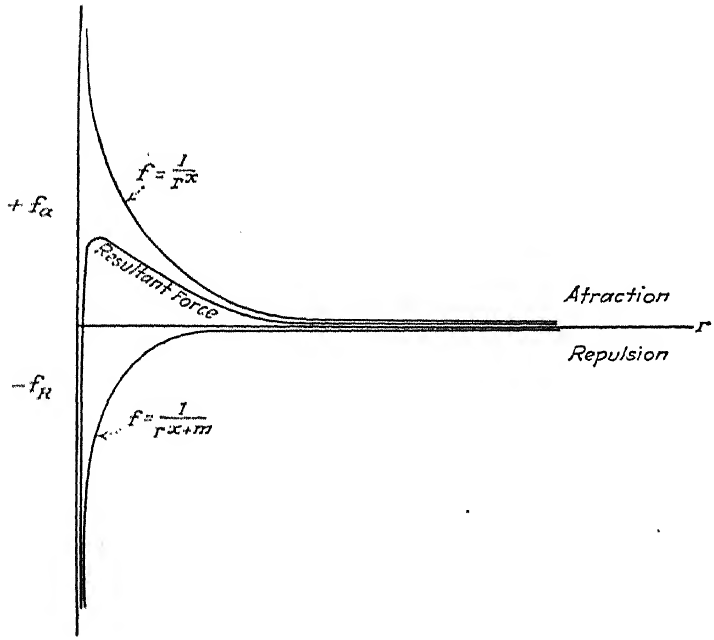

FIG. 30.

One may well ask how it is that the molecules can at the same time exert attractive forces of cohesion and repulsive forces at impact. The explanation is very simple. All that is required is that the forces decrease with the distance at different rates. For example, if the attractive forces of cohesion varied as $f_a = \frac{k}{r^x}$ while those of repulsion varied as $f_R = \frac{k'}{r^{x+m}}$, then the forces could be plotted as functions of r at different distances, as in Fig. 30. In this case the repulsive forces are negative while the attractive forces are positive. It is seen that at first the attraction predominates over repulsion up to the point where the curve intersects the axis. At this point repulsion becomes the greater.

If the particles were at rest close to each other they would approach to the distance r given by the point of intersection and remain there. If there was relative motion, the particles might approach more closely (*i.e.*, until the kinetic energy of the particle equaled the potential energy due to repulsion). The value of σ would be given by the value of r at the latter point. The so-called radius will, in general, however, not be far from the point where attraction and repulsion are equal, because the real powers of r, x, and $m + x$ are much greater than those assumed, as will be seen in a later chapter[10] (Sec. 64).

It is thus clear that the simplifying assumptions made by Van der Waals, *i.e.*, the constancy of a and b, are inaccurate, for a and b should and do vary with T and v. The failures of the theory are thus to be attributed to these causes rather than to its being an erroneous theory. Attempts to improve it which are not purely empirical must endeavor to take account of these changes, and the extent of success achieved will form the body of Sec. 54. Even with this crude assumption, however, the theory has succeeded very well in giving an orienting picture of the equation of state of a real gas, and the uncertain values of a and b serve very useful purposes in helping to account for gaseous behavior.

53. The Joule-Thomson Effect Interpreted by Van der Waals' Equation.—The values of the constants a and b of Van der Waals' equation may be determined in still another fashion. This is by means of the so-called "porous-plug" experiment of Joule and Thomson. Inasmuch as the interpretation of this effect by means of Van der Waals' equation leads to a clear explanation of an otherwise complex phenomenon, it is of considerable value to give the analysis.

If a gas expands by a volume v against an outside pressure p it does work equivalent to the product pv. The energy for doing this work comes from the heat energy (*i.e.*, the kinetic energy of the gas molecules). The expanding gas then does work but loses heat energy in the process. If the process is so conducted that no heat flows in, the gas is cooled. This external work performed would be the only work performed by an ideal gas. In a real gas, however, the molecules attract each other and the expansion of the gas against the internal pressure also consumes energy. In this case the gas would also be cooled and the work it did would result in increasing the potential energy of the gas, for

if the gas were left to itself so that the attracting forces alone could act it would contract and the work of contraction would again come out as increased heat energy of the molecules. Thus for real gases an expansion against external pressure would result in a cooling, due to two causes—one the external work done, the other the work done against the internal pressure. To see whether the ideal gas law held or whether there were internal forces of attraction, Gay-Lussac performed the following experiment: Two carefully heat-insulated vessels A and B of Fig. 31 were connected by a valve V. One was filled with compressed air, the other was evacuated. A thermometer was placed in each. When they had reached the room temperature the valve

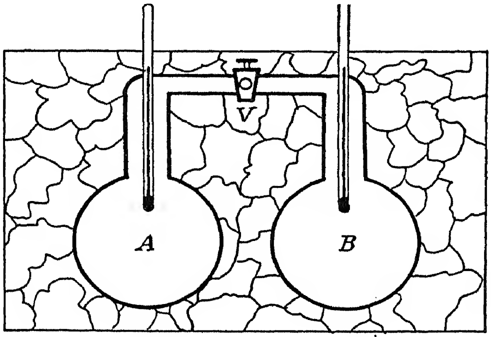

FIG. 31.

was opened and the air in A flowed into B. After the first air had entered B the succeeding air expanded from A and compressed the air in B. If the process was done so quickly that heat did not flow into or out of the system, the air in A should have cooled and the air in B should have been warmed by the work of compression. Since the heat of compression in B came from the heat which was present in the gas in A, no loss or gain from the environment having occurred, the heating in B should equal the cooling in A if no internal work was done. If work had been done against molecular attractions, then, since before expansion the gas had the volume A while afterwards it had the volume $A + B$, there should have been a cooling due to the internal pressure p' acting against the expansion from A to $A + B$. The gain in heat in B plus the loss in heat in A should not then have equaled zero, but should have been less than zero, by an amount depending on the specific heat of the gas, the volume changes, and the

magnitude of the $p' = \frac{a}{v^2}$ pressure term of intermolecular attractions. Since $\frac{a}{v^2}$ is small and since the thermometers available to Gay-Lussac had a high heat capacity and were inaccurate, it was to be expected that he found the sum of the temperatures in A and B equal to zero.

A similar result was also obtained by Joule. In this experiment the vessels A and B were placed in a water bath. Thus if the heating in B were less than the total cooling due to the expansion in A and the work against the internal pressure, the net cooling should have lowered the temperature of the bath. Again, because of the large heat capacity of the bath and the inadequacy of his thermometers, no cooling was observed.

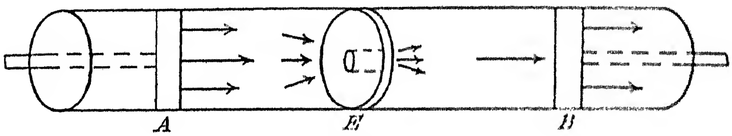

FIG. 32.

Later Joule again attacked the problem with the help of Sir W. Thomson, Lord Kelvin. On this occasion they used a method involving the continuous expansion of the gas through a porous plug of cotton wool. In this instance they obtained a positive result and the experiment has become famous in history as the Joule-Thomson "porous-plug" experiment.

The theory of the method is as follows: Consider a cylinder with a partition E in which there is a small hole. Also imagine two pistons A and B, one on each side of the partition E in Fig. 32. If a gas be in the volume AB and the piston A be moved in slowly, the air in AE will be compressed. As a result, it will flow through E into EB. If B be connected to some mechanism so that it exerts a constant pressure on the gas E which is less than the pressure on A, the gas will flow from AE to EB and will move B outward, that is, it will do external work on B. Experimentally, this is accomplished by letting air in an external reservoir flow through a small opening continuously; the pressure difference between AE and EB causing the flow, and the pressure in EB giving the constant back pressure. If O is the area of the cylinder then p_1O is F_1, the force on A, and p_2O is F_2, the force on B. If A moves x_1 cms and B moves x_2 cms then the work done is

$F_1x_1 = p_1Ox_1 = p_1v_1$. Likewise, $F_2x_2 = p_2Ox_2 = p_2v_2$. After this process the work done on the gas is p_1v_1 and that done by it is p_2v_2. If the initial internal energy in A per unit mass of gas was U_1 and the final internal energy of the gas per unit mass of gas in B was U_2, then, by the law of conservation of energy, the energy change per unit mass of gas is given by

$$Q = -U_1 + U_2 - p_1v_1 + p_2v_2.$$

The convention of signs used in this equation, and in what follows, makes the work done *by* the gas *positive* and that done *on* the gas *negative*. U_2 is greater than U_1, for the gas has gained internal energy, and $U_2 - U_1$ is positive, for it is the work done by the gas in expanding against its internal pressure. It now becomes necessary to evaluate U_1, U_2, p_1v_1, and p_2v_2 by the use of Van der Waals' equation for a real gas.

$$U_2 - U_1 = \int_{v_1}^{v_2} pdv = \int_{v_1}^{v_2} \frac{a}{v^2}\,dv = -a\left(\frac{1}{v_2} - \frac{1}{v_1}\right).$$

Writing the equation for the gas in AE and EB,

$$\left(p_1 + \frac{a}{v_1^2}\right)(v_1 - b) = RT_1$$

and

$$\left(p_2 + \frac{a}{v_2^2}\right)(v_2 - b) = RT_2.$$

Hence

$$p_1v_1 + \frac{a}{v_1} - bp_1 - \frac{ab}{v_1^2} = RT_1$$

and

$$p_2v_2 + \frac{a}{v_2} - bp_2 - \frac{ab}{v_2^2} = RT_2.$$

Combining these to get $p_2v_2 - p_1v_1$,

$$p_2v_2 - p_1v_1 = -\left(\frac{a}{v_2} - \frac{a}{v_1}\right) + b(p_2 - p_1) + ab\left(\frac{1}{v_2^2} - \frac{1}{v_1^2}\right) + R(T_2 - T_1).$$

Now ab is a small quantity of the second order, and so may be neglected. The expression for Q then becomes

$$Q = U_2 - U_1 + p_2v_2 - p_1v_1 = -2a\left(\frac{1}{v_2} - \frac{1}{v_1}\right) + b(p_2 - p_1) - R(T_1 - T_2).$$

To reduce the expressions in v into terms of p for practical use in the equation, the *ideal* gas relation $pv = RT$ may be utilized, for $\frac{1}{v_2} - \frac{1}{v_1}$ is a difference of the first order. An ideal gas

differs from these by one part in a thousand or so. The error introduced in the difference between these two quantities expressed in terms of the pressure would be made one-tenth of 1 per cent by neglect of the corrections, since both v_1 and v_2 are volumes differing by a large amount. Thus $v_2 = \dfrac{RT_2}{p_2}$, and $v_1 = \dfrac{RT_1}{p_1}$ and the expression $2a\left(\dfrac{1}{v_2} - \dfrac{1}{v_1}\right)$ becomes

$$2a\left(\frac{p_2}{RT_2} - \frac{p_1}{RT_1}\right) = \frac{2a}{R}\left(\frac{T_1p_2 - T_2p_1}{T_2T_1}\right).$$

Now T_1 and T_2 differ by only a minute amount, as the early experiments of Gay-Lussac and Joule showed. In fact, $T_1 - T_2$ is of the order of 0.2°C. The factors multiplying p_2 and p_1 are of the order

$$\frac{273.2p_2 - 273.0p_1}{(273.2)(273.0)}.$$

An error of less than one-tenth of 1 per cent would be introduced in this quantity by writing this $\dfrac{(p_2 - p_1)}{T}$, where T could be chosen as the average value between T_1 and T_2. Thus

$$a\left(\frac{1}{v_2} - \frac{1}{v_1}\right) = \frac{a}{RT}(p_2 - p_1).$$

Therefore Q is given by

$$Q = -\frac{2a}{RT}(p_2 - p_1) + b(p_2 - p_1) - R(T_1 - T_2) =$$
$$\left(\frac{2a}{RT} - b\right)(p_1 - p_2) - R(T_1 - T_2).$$

Now per unit mass of gas $Q = JC_v(T_1 - T_2)$, where J is the mechanical equivalent of heat and C_v is the specific heat at constant volume. Thus each unit mass of gas which goes from AE to EB is cooled or heated by $T_1 - T_2$, and as it has a specific heat C_v, the heat consumed in raising that mass from T_1 to T_2 is $(T_1 - T_2)C_v$. Since the right-hand side of the equation is in work units, Q must be multiplied by J to make the equation uniform. Also an ideal gas has $C_p - C_v = \dfrac{R}{J}$, and in this experiment, since the gas is expanding, it is C_p which is needed. The error produced by using this approximation is negligible, for the heat consumed in overcoming molecular forces is small compared to the external work involved. Accordingly, the equa-

tion can have Q replaced by $Q = JC_v(T_1 - T_2) = -\frac{R}{J}(J)$ $(T_1 - T_2) + JC_p(T_1 - T_2)$
and one obtains

$$-R(T_1 - T_2) + JC_p(T_1 - T_2) = \left(\frac{2a}{RT} - b\right)(p_1 - p_2) - R(T_1 - T_2)$$

or
$$JC_p(T_1 - T_2) = \left(\frac{2a}{RT} - b\right)(p_1 - p_2),$$

that is,
$$\frac{\Delta T}{\Delta p} = \frac{T_1 - T_2}{p_1 - p_2} = \frac{1}{JC_p}\left(\frac{2a}{RT} - b\right).$$

This equation says that if the gas in AE at a pressure p_1 be allowed to expand against a pressure p_2 in EB there will be a difference of temperature $T_1 - T_2$ set up on the two sides of E whose value is given by $\frac{1}{JC_p}\left(\frac{2a}{RT} - b\right)$, where a and b are the Van der Waals' constants, T is the absolute temperature, R the gas constant referred to the units in which a and b are expressed, C_p is the specific heat at constant pressure, and J is the mechanical equivalent of heat.

It is now of interest to discuss this result. According to the equation, the difference in temperature should be directly proportional to the difference in pressure. For pressure ranges which are not too great, this holds quite well. For higher pressures, the neglect of some of the terms in the derivation lead to a disagreement which is taken care of in a more perfect equation to be studied later. Furthermore, it should vary with $\frac{1}{C_p}$, which is not surprising, for the higher C_p the less the rise in temperature produced by a given amount of work. If $\frac{2a}{RT}$ is greater than b the gas should be cooled, for $T_1 - T_2$ will be positive, indicating that T_1 is greater than T_2. For some gases where b is larger than a, one obtains $T_1 - T_2$ negative, that is, a heating of the gas. It is obvious also that for high values of RT the $\frac{2a}{RT}$ will be less than b. Hence the effect should show a reversal in sign on reaching a certain temperature. The value of T for this reversal (the inversion temperature T_i) is given by setting

$$\frac{2a}{RT_i} = b \text{ or } T_i = \frac{2a}{Rb}.$$

These conclusions may now be tested by comparison with experiment. Since a and b are usually expressed in cm^6 $\times$ atmospheres, and cm^3 it is necessary to transform the equation to the proper units. C_p, which is given per gram of gas, must be multiplied by ρ, the density of the gas. J, which is in ergs, must be converted into cm^3 $\times$ atmospheres by division by 1.013×10^6. R is in this case $1/273$ for $RT_o = 1$ when $p = 1$ atmosphere and $v = 1$ cm^3. The equation then is

$$\frac{\Delta T}{\Delta p} = \frac{T_1 - T_2}{p_1 - p_2} = \frac{0.0242}{\rho C_p}\left(\frac{2a}{\frac{T}{273}} - b\right)$$

For CO_2, $a = 0.00874$, $b = 0.0023$, Van der Waals' values for Regnault's data taken at low pressures, comparable with the experiments for ΔT of Joule.

$$C_p = 0.000399,\ T = 273.$$

Therefore $\frac{\Delta T}{\Delta p} = 0.925$, Joule observed $\frac{\Delta T}{\Delta p} = 1.05$.

For air, taking $a = 0.00257$ and $b = 0.00156$ from critical data, using $C_p = 0.000307$ and $T = 273$, one obtains $\frac{\Delta T}{\Delta p} = 0.274$, Joule observed a mean $\frac{\Delta T}{\Delta p}$ of 0.259 with values ranging from 0.244 to 0.288. For H_2 gas in which b is greater than a, using more recent values for a and b given by Jellinek,[12] and transformed to fit the equation as here given, one has $a = 0.00038$, $b = 0.001025$, $C_p = 0.000305$, and $T = 273°$ abs. These give

$$\frac{\Delta T}{\Delta p} = \frac{(T_1 - T_2)}{(p_1 - p_2)} = -0.029.$$

Joule observed a value of $\frac{\Delta T}{\Delta p} = -0.039$, that is, the gas was heated on the side EB by an amount equal to 0.03°C. above the side AE per atmosphere temperature difference.

From the values for a and b the inversion temperature T_i of this heating effect can be estimated for H_2.

$$T_i = \frac{2a}{Rb} \text{ or } T_i = \frac{2a}{b}\,273° \text{ abs.}$$

$$T_i = \frac{0.00076}{0.001025}\,273° = 202° \text{ abs., or } -71°\text{C.}$$

Hence, at -71°C. the heating effect in hydrogen should change to a cooling effect. Actually, Olszewski[12] found a reversal at -80.5°C.

All these results show that, in general, there is agreement between the observed and theoretical values. Again, as in the critical constants, the effect depends on differences of small variable quantities. Thus the numerical agreement is not entirely satisfactory. Further errors are introduced by the simplifying assumptions used. A careful thermodynamic treatment of the case, to which the reader is referred to Jellinek[13] gives the more exact result that

$$\frac{dT}{dp} = \frac{\left(\frac{\partial v}{\partial T}\right)_p - v}{C_p}$$

Writing Van der Waals' equation in the form

$$v = \frac{RT}{p} - \frac{a}{pv} + \frac{ab}{pv^2} + b$$

and simplifying it by replacing pv by RT,

$$v = \frac{RT}{p} - \frac{a}{RT} + \frac{abp}{R^2T^2} + b$$

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p} + \frac{a}{RT^2} - \frac{2abp}{R^2T^3}$$

and

$$T\left(\frac{\partial v}{\partial T}\right)_p - v = \frac{2a}{RT} - \frac{3abp}{R^2T^2} - b.$$

Thus

$$\frac{dT}{dp} = \left(\frac{2a}{RT} - \frac{3abp}{R^2T^2} - b\right)\frac{1}{JC_p}.$$

This differs from the former equation in that it has the negative term $\frac{3abp}{R^2T^2}$ in it. Thus for large values of p, $\frac{dT}{dp}$ should decrease with increasing pressure, as it is observed to do. $\frac{dT}{dp}$ becomes zero for the condition that $\frac{2a}{RT} - \frac{3abp}{R^2T^2} - b = 0$. This is a quadratic equation in T and there are thus two temperatures at a given pressure at which the effect disappears. This makes the pressure temperature curve for the disappearance of the Joule-Thomson effect a parabola and its course is more complicated than the simple theory which holds only for low pressures requires.

The Joule-Thomson effect is also used in determining that temperature on the Centigrade scale which represents the

absolute 0 of temperature. The method is, however, thermodynamical and finds no place in this text.

54. Other Equations of State.—As has been seen, Van der Waals' equation is but a first-order approximation. Its imperfections have spurred various workers on to improve its agreement with experiment. In studying the improvements proposed, one might, with Jeans,[14] use two deviations as criteria in discussing the equations. It was found in Sec. 52 that $v_c = 3b$ for gases from Van der Waals' equation. In general, v_c is more nearly $2b$. Also it should follow from the theoretical values of p_c, v_c, and T_c that $p_c v_c = \frac{3}{8} R T_c$. Actually, RT_c is more nearly $3.7 p_c v_c$ than $2.66\, p_c v_c$ as the theory demands.

It is possible to write Van der Waals' equation in another form known as the "reduced equation of state." If for the variables p, v, and T one substitute the variables P, V, and T_1 related to p, v, and T by $T_1 = \frac{T}{T_c}$, $P = \frac{p}{p_c}$, $V = \frac{v}{v_c}$ then from the values of the critical constants (Sec. 52) one obtains Van der Waals' equation in the form

$$\left(P + \frac{3}{V^2}\right)\left(V - \frac{1}{3}\right) = \frac{8}{3} T_1.$$

This equation is the same for all gases, for the characteristic constants a and b have been eliminated. It is merely necessary to find p_c, v_c, and T_c to express the equation in the reduced form.

There are two ways in which the improvements of Van der Waals' equation have been attempted. The first is by means of added constants of an empirical nature. The second is by the more rigorous deduction of the equation allowing for temperature and other variations of a and b.

With the relations above in mind, one may go to a typical attempt to modify Van der Waals' equation to agree with facts more closely by the use of empirical relations. Kammerlingh-Onnes[18] uses a quantity K defined by the relation $K = \frac{RT_c}{p_c v_c}$, which characterizes the deviation from Van der Waals' equation as suggested above. This K is dimensionally a pure number. Calling $V_k = \frac{V}{K}$ the Van der Waals' equation above in this new notation reduces to

$$\left(P + \frac{27}{64 V_K^2}\right)\left(V_K - \frac{1}{8}\right) = T_1.$$

This can be transformed into

$$PV_K = \frac{T_1}{1 - \dfrac{1}{8V_K}} - \frac{27}{64V_K}.$$

which expands into

$$PV_K = T_1\left\{1 + \frac{1}{V_K} + \left(\frac{1}{8} - \frac{27}{64}\frac{1}{T_1}\right) + \frac{1}{64V_K^2} + \frac{1}{512V_K^3} + \cdots\right\}.$$

This equation is, however, not satisfactory even when the experimental value of K has been introduced, for it was seen that it was not only the position of the theoretical isotherms but their actual shapes which deviated from the observed ones. In other words, making the critical isotherm agree in one point with experiment did not insure agreement of the other isotherms. Kammerlingh-Onnes *assumed* a purely empirical form of the equation above and wrote it

$$PV_K = T_1\left(1 + \frac{B}{V_K} + \frac{C}{V_K^2} + \frac{D}{V_K^4} + \frac{E}{V_K^6} + \frac{F}{V_K^8}\right)$$

where B, C, D are themselves series of the from

$$B = b_1 + \frac{b_2}{T_1^2} + \frac{b_3}{T_1^2} + \frac{b_4}{T_1^4} + \frac{b_5}{T_1^6} + \cdots$$

This gives at least 25 adjustable constants. Such an equation has no basis in theory. With as many constants it should be possible to obtain close agreement with any observed curve. For a discussion of the success of this equation one may be referred to Jeans.[14] It serves as an example of one of the most successful attempts at an accurate empirical representation.

Clausius[15] attempted an empirical modification of Van der Waals' equation. This takes the form

$$\left(p + \frac{a'}{T(v + c)^2}\right)(v - b) = RT.$$ ✓

He introduces in place of the old constant a a new constant a', which is divided by the absolute temperature. Thus he makes the old a inversely proportional to the absolute temperature. Besides this, an adjustable constant c is added to the v in the expression for the internal pressure of Van der Waals. The introduction of a temperature correction into a is not quite empirical, for a is theoretically expected to depend on temperature. This correction alone improves the fit of Van der Waals' equation to the data leaving c out. Better agreement is obtained for a properly chosen c. The formula fits Andrews' results in

CO_2 better than the original equation at high densities; at low densities it gives a poorer fit. For other gases it is even less successful. Clausius then devised a still more elastic equation containing one more constant and putting an undetermined exponent on the temperature correction. These gave better fits for some gases, as was to be expected, but again failed when extended to more gases. Thus it appears that the agreements of empirical equations obtained by extending Van der Waals' equation can, by choosing enough constants, be made to fit experimental data more or less accurately. They, however, teach nothing about the phenomena and do not suggest further investigation. They serve a useful purpose in expressing the true behavior of a gas in a condensed and serviceable form which permits of the introduction of such accurate relations into applications demanding the relations which they yield.

Two attempts at a theoretical improvement of the equation of state applicable to limited ranges of volume have met with a success that merits discussion. The first attempt results in an equation first empirically proposed by Dieterici which has now been placed on a rigorous theoretical basis by Jeans.[16] The latter deduces this equation from a generalized calculation of the gaseous pressure. This general expression for the pressure is of an exceedingly complex character, involving the molecular densities due to different conditions existing. Jeans evaluates the expression for the gas pressure, assuming spherical molecules having a definite diameter σ. He allows for the existence of forces of cohesion, the method of attack involving a study of the changes in molecular densities at and near the surface of the gas produced by these forces. Making certain approximations he arrives at the expression $p = \frac{RT}{v - b} e^{-\frac{a}{RTv}}$ which is Dieterici's equation. It is seen that it is the same as Van der Waals' equation except that the $p + \frac{a}{v^2}$ is now replaced by $pe^{\frac{a}{RTv}}$. This equation gives Van der Waals' equation when a and b are small. Theoretically, as Jeans points out, this equation has a range of validity no better than Van der Waals' equation at great pressures. It gives for v_c, however, a theoretical value of $2b$, which is more nearly in accord with experiment, while $K = \frac{RT_c}{p_c v_c} = \frac{1}{2}e^2$, or 3.695, which fits the experimental values more closely than does the value 2.66 from

the original equation of Van der Waals. In fact, it was to obtain these numerical relations that Dieterici set up his original equation, this equation being the best of several proposed. It agrees with the data for isopentane well for pressures less than 12 atmospheres, and holds fairly well beyond this range. In general, it is numerically slightly more satisfactory than the original Van der Waals' equation, although it is far from correct.

Finally, Reinganum,[17] using the theorem of the virial, much as it was deduced in Sec. 50, carried the considerations for gases at moderately high pressures further by putting in corrections for b and a with temperature. This was accomplished through taking account of the relation of the energy of the heat motions and the potential energies of the molecules due to the forces of cohesion and repulsion in evaluating the virial. The processes by which this is accomplished fit in readily with the development of Sec. 50, but are too lengthy to reproduce at this place. They will be found in Jaeger's[5] "Fortschritte der Kinetischen Gas Theorie," as well as in Jellinek, vol. 2. The resulting equation takes the form

$$pv = RT\left(1 + \frac{be^{\frac{c}{T}}}{v}\right) + \frac{2\pi n^2}{3v}\phi(T).$$

If $\frac{be^{\frac{c}{T}}}{v}$ be considered small compared to 1, division by the term $1 + \frac{be^{\frac{c}{T}}}{v}$ gives a close approximation to the equation above in the form $\left(p - \frac{2n^2\phi(T)}{3v^2}\right)(v - be^{\frac{c}{T}}) = RT$. An analogous approximation was made with $v + b$ in the deduction of Sec. 50.

Thus $-\frac{2\pi n^2\phi(T)}{3}$ is the equivalent to Van der Waals' a, and $be^{\frac{c}{T}}$ is the equivalent to Van der Waals' b. This new expression merely, therefore, accounts for the theoretical value of a and for the variation of a and b with temperature. The way in which the term equivalent to a varies with temperature is undefined and is left to experiment to determine for each gas. The variation of b with temperature is fixed except for the knowledge of the constant c, which remains to be determined for each gas by experiment. The equation has the disadvantage over Dieterici's equation in that it has one more undefined constant and an undefined func-

tion of the temperature. It should, therefore, be more easily fitted to the results than the latter equation and is perhaps a bit more accurate. The volume correction for a or b is absent in this equation, for it must be remembered that the expression was deduced to hold only for conditions where pressures were relatively low. It contains this condition in the specific assumptions that at no time more than two molecules should be close enough together to exert powerful forces on each other.

The last two equations thus give the best theoretical attempts at extending Van der Waals' equation and hold for relatively low pressures. As is seen, these are not especially successful, and it might be assumed that the complications introduced by their use in practical applications more than offset any advantages gained. They are, however, substantial advances and must be so regarded.

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CHAPTER VI

TRANSFER OF MOMENTUM, TRANSFER OF ENERGY, TRANSFER OF MASS THROUGH A GAS. THE KINETIC THEORY OF THE COEFFICIENTS OF VISCOSITY, HEAT CONDUCTION, AND DIFFUSION

55. Introduction.—In Chap. III it was shown that, in spite of their high speeds, gas molecules liberated at one point in a space did not instantaneously appear at points at moderate distances from the origin. The reason for this was shown to be due to the effect of collisions with the myriads of molecules present in unit volume which prevented a molecule traveling for more than a very short distance in any given direction. This led at once to the concept of the mean free path, which was discussed in detail in that chapter. The correctness of this concept was there demonstrated by direct measurements of the mean free path and distribution of free paths all of more or less recent date. When the kinetic theory was developing, the experimental technique and the knowledge in such fields as electronics had not developed to the extent necessary to permit these verifications. In fact, no direct test of the mean-free-path concept was then possible. In attempting to demonstrate the correctness of the hypothesis, it was natural that the workers should have turned for its verification to the striking discrepancy with the notion of rapidily moving molecules (*i.e.*, the slow diffusion and heat transfer) which had led to the mean-free-path concept. Thus at a very early date the three phenomena depending on molecular velocities and free paths which could throw light on the low values of the latter were carefully analyzed. These three phenomena depend on the transfer of matter, of momentum, and of energy through a gas. They lead in an experimental study to three constants depending on the nature of the gas, called the coefficients of diffusion, viscosity, and heat conduction.

The analysis of these three constants from the kinetic-theory point of view led to predicted variations of the constants with pressure, temperature, and masses of the molecules, some of which were at the time unknown, whose verification afforded a

striking proof of the correctness of the assumptions involved. They also led to predicted relations between the coefficients of heat conduction and viscosity, which were found to be approximately correct. Some of the predictions, notably the temperature variations, were not fulfilled. Where this was the case, it was found that the theoretical simplifications and some of the assumptions (*e.g.*, that of the independence of molecular diameters of the temperature) were not strictly true, and that to this extent the theory had to be modified.

The deductions also led to relations which enabled the mean free paths of the molecules L to be evaluated. These values are in excellent agreement in order of magnitude with those estimated from the Van der Waals' equation (Chap. V) and from the more direct measurements of Chap. III. The lack of complete numerical agreement must be ascribed to two causes: first, to the fact that, as the free path L is a function of the temperature, the results of the measurements are not strictly comparable (*e.g.*, as in the electron free paths, where the velocities were notably higher than those for ordinary molecular impacts, and the values of the diameter as deduced from the coefficient of viscosity η); and second, to the uncertainty as to the value of the numerical constants resulting from differences in the manner of averaging the velocities (*e.g.*, the Maxwell and Tait free paths (Sec. 39) or Jean's persistence of velocities).[1] At the time, however, the agreement between theory and experiment was most striking, and today, in spite of the more complicated analysis necessary for a satisfactory treatment, the study of these coefficients in the light of the kinetic theory furnishes an inspiring example of this type of analysis. It is the purpose of this chapter to give both the elementary treatment of the problems and some of the later, more accurate findings. For the proper treatment of the subject, it seems best to derive the expressions in an order which places the coefficient of viscosity first, heat conduction second, and diffusion last, because of the relative mathematical simplicity of the cases of viscosity and heat conduction compared to diffusion. The chapter will be divided into three parts: Part I, Coefficient of Viscosity; Part II, Coefficient of Heat Conduction; Part III, Coefficient of Diffusion.

56. Irreversible Phenomena.—Before proceeding to a discussion of Parts I, II, and III, it is of interest to point out a marked difference in the case of these phenomena compared to the

phenomena which formed the basis of the discussions of all previous chapters. In those chapters the discussion was limited chiefly to the cases of gases in equilibrium. In such cases the temperature and the partial pressure of the gases remained constant throughout. In fact, the deductions of Chap. IV depended on this equilibrium. Thus in the cases treated there was no streaming motion in the gas and one part of the gas was like another part as regards constitution, momentum, and energy distribution. Part I and the following parts deal with gases which are not in equilibrium and which are striving to attain that state.

It is a fact of common experience that, if a gas is set in motion in its container, the motion will be gradually dissipated until the temperature and the pressure of the gas are uniform throughout and there is no directly observable motion in the gas. The phenomenon of the dissipation of internal motion is known as "viscosity." It is perhaps the simplest of the irreversible phenomena.

Again, if the gas in a container is not at a uniform temperature throughout, differences of density arise, and so, owing to the buoyant action arising from gravitational force and governed by Archimedes' principle, convection currents arise. These motions are dissipated by viscous friction, and so, ultimately, temperature, equilibrium is attained. But there is a more direct process by which the temperature equilibration is carried out, and which is present in arrangements where convectional streaming is prevented. This process is that of heat conduction.

The third principal irreversible phenomenon is that of diffusion. In this a gas consisting of a mixture of different varieties, the composition of which is initially variable from point to point, gradually becomes uniform. As different gases do not have the same density at the same temperature and pressure, there is also convective action which results in mixing when the gas is, as is usually the case, in a gravitational field. The phenomenon of diffusion, properly speaking, is, however, one which takes place independently of this convective action. It is due, as are the other two real processes, viscosity and heat conduction, to the eternal and chaotic random heat motions of the molecules.

The designation "irreversible" for these phenomena arises from the fact that all three are conditioned by the second law of thermodynamics, being processes in which the energy is degraded

(*i.e.*, in which the molecular chaos ("mixed-upness") of the universe is increased). It is important to note that the second law of thermodynamics tells merely the *direction* of the phenomena—that is, that the streaming motions will be dissipated, that the temperature will become uniform, and that the composition will become uniform. Thermodynamics does not offer any information about the time rate, or speed, with which these processes take place. Experiment and the kinetic theory, by giving information about the time rates of these phenomena, thus make a great advance over the doctrine of energetics.

I. VISCOSITY

57. The Experimental Definition of Viscosity.—Consider a gas in a container having plane parallel walls infinite in extent. Assume, now, that one of these remains fixed while the other one moves relative to it with a velocity u. Let the distance between these two walls be z. An arrangement of this sort could be realized experimentally by having the moving wall a long, flat belt moving endlessly over two rollers, and considering a small region far from the rollers. Experiment has shown that the gas will be set in motion in the direction of the moving belt, that it will be at rest relative to each boundary, at the boundary (except for a slight slipping to be discussed later), and that the motion of the gas between the plates will fall off linearly from the moving plate to the fixed one—that is, the gas next the moving plate will be set into motion by it, momentum being lost by that plate in transmitting motion to the gas. The outer layer of gas will then set the next inner layer into motion, suffering thereby a loss of momentum, so that its velocity will be less than that of the plate. Thus a gradient of velocity will be set up across the gas space, which experiment shows is a linear one. If the velocity of the layer of gas at the plane $z = 0$ is designated as 0, and at $z = z_0$ as u_0, the rate of increase of speed with z, or the velocity gradient, is $\frac{u_0}{z_0}$. When the steady state of motion is reached, the upper plate is losing momentum to the gas, and as a result experiences a viscous force or drag which is equal to the rate of loss of momentum. Thus the viscous force of the gas is measured by the rate of change of momentum involved.

Experimentally, it was found that the force was proportional to the area of the moving plane exposed to the gas, and to the

velocity gradient in the gas. That is, if f be the force on the plane, A its area, and $\frac{du}{dz}$ the velocity gradient, then

$$f = -\eta A \frac{du}{dz},$$

and if F be the force per unit area,

$$\frac{f}{A} = F = -\eta \frac{du}{dz}.$$

Here η is a constant of proportionality characteristic of the gas, the coefficient of viscosity. The negative sign denotes that the force opposes the motion u. It is the significance of η in terms of the molecular quantities which it is desired to derive from the kinetic theory. In the c.g.s. system of units η gives the force in dynes per cm² acting on the surface when the velocity gradient is 1 cm/sec. in a cm taken normal to the surface, *i.e.*, along the z-axis. To orient oneself, it may be of interest to note that η for air is 1.8×10^{-4} dynes/cm² per unit gradient, while η for H_2 is 0.9×10^{-4}, η for water is 0.01 at 20°C., and η for glycerine is 8.5 at 20°C. In mentioning the value of η for liquids whose definition and experimental measurement are precisely the same as for those of gases, it becomes essential to point out a fundamental difference between the interpretation of η for the two classes of substances on the kinetic theory. In gases the intermolecular forces are considered as completely negligible, or at least relatively small, in their effects compared to the peculiar type of transfer assumed. In liquids, the intermolecular forces, as evidenced by cohesion, play an entirely dominating rôle. Hence viscosity in liquids is largely governed by cohesive forces and shows little dependence on density, molecular velocity, or mean free path. It is, therefore, not surprising that liquids whose cohesive forces rapidly become weakened as temperature increases should show *reduced viscosity* with *increasing* temperatures. In gases where, as will be seen, the viscosity depends on the rate of transfer of momentum, the viscosity *increases* as temperature increases.

58. The Simple Kinetic Analysis of Viscosity.—The first analysis of η from the point of view of the kinetic theory was due to Maxwell in 1860.[2] From the discussion of the previous section, it was evident that the viscous drag exerted by the gas on the plane was due to a loss of momentum of the plane to the gas. This transfer of momentum from the faster layer to the adjacent

slower layer was then found to take place throughout the gas, leading to the establishment of a velocity gradient from one plate to the next. It also leads to the manifestation of a viscous drag on the stationary plane which could be detected by a suitable measuring device, showing that some of the momentum of the moving plane is being transmitted through the gas to the fixed plane.

This transfer of momentum through the gas may be pictured by the kinetic theory in the following fashion: According to the distribution law, the molecules are moving in the gas in a completely random fashion with average velocity components equal along the three axes. The streaming motion of the gas merely indicates that there is a minute average additional velocity of all the molecules in the given directions. This additional velocity, a few cm/sec, is so small compared to C (about 40,000 cm/sec) that it may be assumed to be of little influence on the Maxwellian law of distribution. If the velocity gradient exists in the gas, the molecules in one of the upper, more rapidly moving layers (that is, one having a small additional component u_1 in the x direction) will move from this layer to one of the lower and slower layers, carrying with it its initial component u_1 in the x direction. If in this lower layer where the speed of the molecules along the x direction is lower (*i.e.*, where the average velocity of the molecules in the x direction is $u_2 < u_1$) the first molecule suffers collision, its added momentum will be given up to the lower layer. Thus the lower layer will move faster as a result of this. On the other hand, some molecules from the lower layer will, by their heat motions end in the upper layer, and being slower, will decrease the average momentum of the molecules in the upper layer. It is then by such a process that the momentum is transferred from layer to layer of a gas and it is from a precise analysis of this process that it should be possible to derive the expression for η.

To this end the following simple assumptions may be made: Let it be assumed that an average molecule traverses a distance equal to the mean free path between impacts. The length of this path is then a rough measure of the thickness of the layer of gas in which viscous action occurs. On the two sides of a layer of gas L cm thick, whose plane is parallel to the plates, the difference of streaming velocity in the gas is given by $L \frac{du}{dz}$, for the

velocity gradient normal to the motion of the gas is $\frac{du}{dz}$. Thus molecules of mass m coming from the upper side of this layer to the lower side carry an excess of momentum $mL\frac{du}{dz}$ from the upper to the lower side. Now, on the average, one-third of the molecules are moving with paths that are up or down. Thus the number of molecules of speed $\bar{c}$ going up or down across unit area per second will be one-third $N\bar{c}$, where there are N molecules per cm^3. The momentum transferred across this layer up and down by the molecules is thus

$$\frac{1}{3}Nm\bar{c}L\frac{du}{dz}.$$

Now this calculation was made on the assumption of a uniform gradient. This presupposes a steady state.* That means that momentum is being passed on from one layer to the next as rapidly as it is received. Thus the transfer of momentum across the layer L is the same as that given to the gas by the moving plane at z_0 or given to the stationary plane at $z = 0$. This momentum transfer in the gas thus results in a force $-F$ being exerted on the moving plane at z_0, the reaction a force equal in magnitude but opposite in sense being exerted on the lower plane at $z = 0$, of magnitude $+F$. Hence

$$F = \frac{1}{3}Nm\bar{c}L\frac{du}{dz}.$$

By the definition of η, this force $F = \eta\frac{du}{dz}$ per unit area as regards the lower plate. Therefore

$$\eta = \frac{1}{3}Nm\bar{c}L.$$

This equation also follows in exactly the same form from a distinctly more rigorous deduction to be given in the following section. For a discussion of this expression for η as compared with experiment the reader is referred to Sec. 60 at the end of the deduction of this expression.

59. Maxwell's Deduction of the Value of η.—Assume a gas in which a uniform velocity gradient is set up by some adequate

* It is to be observed that by "equilibrium in a gas" is meant uniformity of temperature, velocity, and composition throughout the gas, whereas the term "steady state" merely means that the temperature, velocity, and composition *at a given point do not vary with time.* They may, however, vary from place to place.

experimental arrangement. Choose a point in the gas stream and set up a system of coordinate axes such that the gas moves along the x-axis with a velocity u_o, while the velocity gradient lies along the z-axis. Thus at $z = 0$, u will be u_o. As the velocity gradient is $\frac{du}{dz}$, the velocity at any point $z = z$ will be

$$u = u_o + \frac{du}{dz}z.$$

Owing to this gradient, the molecules which are continually moving from positive values of z through the xy plane are carrying with them momentum corresponding to the region where they

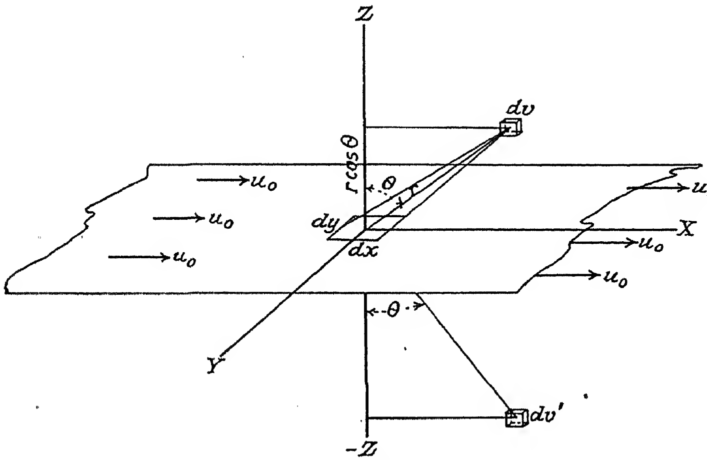

FIG. 33.

last suffered an impact. The validity of this assumption is questioned by Jeans[1] on the basis of his theorem of persistence of velocities. Similarly, the molecules moving from negative values of z are moving through the xy plane, transferring their low momenta along x to the upper layer and decreasing the average momentum of the layer. The net momentum transfer per unit time through unit area gives the force per unit area exerted due to the velocity gradient across the xy plane. To get this, one takes a small element of volume dv (Fig. 33) and finds the rate of transfer of momentum downward through a small area $dxdy$ due to this volume. The same may be done for the upward transfer of momentum through $dxdy$ due to a small volume dv' below the xy plane. By integrating these over all the space above and

below xy the *net* momentum transfer through $dxdy$ per second, and hence the force exerted, may be found.

Assume a small volume dv having N molecules per cm^3 in it. Assume, further, that, on the average, a single molecule experiences $\bar{z}$ collisions in unit time. This quantity may, for purposes of simplification, be considered as $\frac{\bar{c}}{L}$, a constant, where $\bar{c}$ is the average velocity and L is the mean free path. As was seen in Sec. 39, this is really not the case, and in later work the accurate expression for the mean collision frequency will be used. In a time dt the Ndv molecules in dv experience $N\bar{z}\,dv\,dt$ collisions that is to say, in the time dt, $N\bar{z}\,dv\,dt$ molecules start new paths, leaving dv. As all directions are equally probable, the number which leave dv and move towards the small area $dxdy$ is the number of paths starting in dv during dt multiplied by the ratio of the surface cut out by the solid angle subtended at dv by $dxdy$, $dxdy \cos \theta$, to the surface of the sphere of radius r drawn about dv. Here r is the distance from dv to $dxdy$ and θ is the angle the line r makes with the z-axis. Of this number of molecules moving towards $dxdy$, only the fraction $e^{-\frac{r}{L}}$ goes the distance r or more without suffering a collision and being diverted. Thus the total number of molecules leaving dv during dt that pass through $dxdy$ is

$$N\bar{z}\frac{dxdy\cos\theta}{4\pi r^2}e^{-\frac{r}{L}}\,dvdt.$$

Now if, on the average, it is supposed that a molecule possesses the x component of velocity appropriate to the scene of its last collision, each of the above molecules carries an amount of momentum

$$m\left(u_o + r\cos\theta\frac{du}{dz}\right)$$

from dv through $dxdy$. Hence the momentum transfer is

$$-\frac{Nmu_o\bar{z}\,dxdy\,dt}{4\pi}\frac{\cos\theta}{r^2}e^{-\frac{r}{L}}\,dv - \frac{Nmr\cos^2\theta\frac{du}{dz}e^{-\frac{r}{L}}\bar{z}\,dxdy\,dv\,dt}{4\pi r^2}.$$

The negative sign indicates that the momentum is being carried from greater to lower values of z. This quantity must be integrated for r from $r = 0$ to $r = \infty$. It must also be integrated so that dv covers all the space above the xy plane. To do this,

dv must be replaced by $dr(r\sin\theta d\phi)(rd\theta)$ and θ integrated from 0 to $\frac{\pi}{2}$, and ϕ from 0 to 2π. Thus the momentum transfer going through $dxdy$ downward from the space above the xy plane is given by the quantity

$$N_{dxdy\downarrow} = -\frac{Nm\,\bar{z}\,dxdy\,dt}{4\pi}\left[u_o\int_o^\infty e^{-\frac{r}{L}}dr\int_o^{\frac{\pi}{2}}\cos\theta\sin\theta d\theta\int_o^{2\pi}d\phi + \frac{du}{dz}\int_o^\infty re^{-\frac{r}{L}}dr\int_o^{\frac{\pi}{2}}\cos^2\theta\sin\theta d\theta\int_o^{2\pi}d\phi\right].$$

In a similar manner, the momentum transfer from below the xy plane upward from a volume $r^2\cos\theta d\theta d\phi dr$ in a time dt may be found as

$$N_{dxdy\uparrow} = \frac{Nm\,\bar{z}\,dxdy\,dt}{4\pi}\left[u_o\int_o^\infty e^{-\frac{r}{L}}dr\int_o^{\frac{\pi}{2}}\cos\theta\sin\theta d\theta\int_o^{2\pi}d\phi - \frac{du}{dz}\int_o^\infty re^{-\frac{r}{L}}dr\int_o^{\frac{\pi}{2}}\cos^2\theta\sin\theta d\theta\int_o^{2\pi}d\phi\right],$$

the $-$ sign inside the bracket being due to the fact that below the xy plane $u = \left(u_o - r\cos\theta\,\frac{du}{dz}\right)$. Adding the two terms $N_{dxdy\downarrow}$ and $N_{dxdy\uparrow}$ to get the net transfer M, it is found that the first members of the two expressions cancel and there is obtained on integration for the net transfer per unit area per second, *i.e.*, the viscous drag, the quantity

$$\frac{M}{dxdy\,dt} = -\frac{4\pi Nm\bar{z}L^2}{3(4\pi)}\frac{du}{dz} = -\frac{1}{3}Nm\bar{c}L\frac{du}{dz} = -\eta\frac{du}{dz},$$

since

$$\bar{z} = \frac{\bar{c}}{L}.$$

Thus one has

$$\eta = \frac{1}{3}Nm\bar{c}l.$$

This was precisely what was found in the preceding section.

The integration here was carried out assuming $\bar{z}$ to be a constant. Its assumed value $\frac{\bar{c}}{L}$ was the value which one would have obtained using the Maxwell value for the mean collision frequency which is assumed independent of the velocity c as shown in Sec. 39. To take account of the variation, the Tait expression for the mean collision frequency must be used.

The treatment given by Tait, which is the more rigorous one, differs from the one given above only at the point where the integration of the free paths takes place. In this treatment, Maxwell's law of distribution is assumed to hold even though it applies strictly only to equilibrium. However, the quantity which before was written as $\bar{z} = \frac{\bar{c}}{L}$ is no longer so. L is a function of c. If the free path for a given c be taken as l and if one writes for N not a constant N, but N_c, giving the number of molecules with velocities between c and $c + dc$, the equation found above for M becomes

$$M = -\frac{2m\, dxdy\, dt}{4\pi}\frac{du}{dz}\left[\int_0^{\frac{\pi}{2}} \cos^2\theta \sin\theta d\theta \int_0^{2\pi} d\phi \int_0^{\infty} r\bar{z}e^{-\frac{r}{l}}dr \int_0^{\infty} \frac{4N}{\alpha^3\sqrt{\pi}} c^2 e^{-\frac{c^2}{\alpha^2}}dc\right].$$

The integral with respect to θ and ϕ leads to the factor $\frac{2\pi}{3}$. Again, in place of the collision frequency $\bar{z} = \frac{\bar{c}}{L}$, one now writes $z = \frac{c}{l}$, where l is a function of c, which is given by the Tait free-path equation (Sec. 39) as

$$l = \frac{\sqrt{2}\pi\frac{c^2}{\alpha^2}L}{\psi\left(\frac{c}{\alpha}\right)},$$

where L is the Maxwell free path. Thus the equation for $M = N_{dxdy\downarrow} + N_{dxdy\uparrow}$ becomes

$$M = -\frac{1}{3}Nm\, dxdy\, dt\frac{du}{dz}\left[\int_0^{\infty} l^2e^{-\frac{r}{l}}\frac{r\,dr}{l^2}\int_0^{\infty}\frac{4}{\alpha^3\sqrt{\pi}}\left(\frac{c}{l}\right)c^2e^{-\frac{c^2}{\alpha^2}}dc\right]$$

or, calling $\frac{c}{\alpha} = x$,

$$M = -\frac{1}{3}Nm\, dxdy\, dt\frac{du}{dz}\frac{4}{\sqrt{\pi}}\int_0^{\infty}\int_0^{\infty} lcx^2e^{-x^2}e^{-\frac{r}{l}}\frac{r\,dr}{l^2}dx.$$

Integrating this for dr first, setting $c = x\alpha$ and $l = \frac{\sqrt{2}\pi x^2 L}{\psi(x)}$, then

$$\frac{M}{dxdy\, dt} = -\eta\frac{du}{dz} = -\frac{1}{3}Nm\frac{du}{dz}\frac{\alpha L\sqrt{2}\pi}{\sqrt{\pi}}\int_0^{\infty}\frac{4x^5e^{-x^2}dx}{\psi(x)}.$$

This complicated integral was evaluated by Tait and led to the value

$$\int_0^\infty \frac{4x^5\, e^{-x^2}dx}{\psi(x)} = 0.838.$$

Therefore

$$\eta = \frac{1}{3}Nm\alpha(0.838\sqrt{2}L)$$

or

$$\eta = \frac{1}{3}Nm\bar{c}L\left(0.838\sqrt{\frac{\pi}{2}}\right)$$

$$\eta = 1.051\left(\frac{1}{3}Nm\bar{c}L\right),$$

that is, the Tait value for the viscosity is 5.1 per cent higher than the value deduced by the Maxwell form of averaging. Physically, this difference is caused by the fact that the faster moving molecules have longer free paths and thus carry more momentum. This, if taken account of in averaging, as was here done, leads to the viscosity being greater because of the added effect of the longer free paths. Jeans,[1] persistence-of-velocity treatment gives a still greater value for the constant. In this case the ⅓ is replaced by 0.461.

60. Agreement between Elementary Theory and Observation for the Coefficient of Viscosity.—The expression deduced for η, $\eta = \frac{1}{3}Nm\bar{c}L$, with some uncertainty in the value of the constant ⅓ depending on the method of averaging, can be transformed for discussion as follows. Since

$$L = \frac{1}{\sqrt{2}\pi\sigma^2 N}, \quad \eta = \frac{m\bar{c}}{3\sqrt{2}\pi\sigma^2}.$$

1. It is seen at once that, since $\bar{c} \propto \sqrt{\frac{1}{m}}$, η should vary as $\sqrt{m}$. For gases this holds quite accurately if account be taken for the variation of σ, which is comparatively small, for most gases.

2. Furthermore, the expression is independent of pressure, for neither m, $\bar{c}$, or σ is a function of pressure. This surprising relation was deduced before the value of η as a function of pressure had been measured. Investigation[3] showed it to be true for pressures from a few mm of mercury up to several atmospheres, contrary to expectation, for it seemed absurd that the viscous drag of a rarefied gas should be the same as for a dense one. At low pressures the relation fails, since the mean free path then becomes comparable with the dimensions of the apparatus and the assump-

tions used in deducing η no longer hold (see Sec. 77). At very high pressures, where attractive forces between the molecules become appreciable, the relation might again be expected to fail, for momentum transfer of the liquid type begins to occur (see Sec. 64).

3. Again, the $\bar{c}$ above can be replaced by $\sqrt{\frac{8RT}{\pi N_A m}}$, where N_A is the Avogadro number, m the mass of a molecule, R the gas constant, and T the absolute temperature. Thus $\eta = \frac{2}{3\sqrt{\pi}\sigma^2}\sqrt{mkT}$, where $k = \frac{R}{N_A}$, the Boltzmann constant. This predicts that η should vary as the square root of the absolute temperature. Experiment[4] shows that η increases with temperature more rapidly than this and does not follow a power of T. The failure of this prediction to hold depends on the erroneous assumption that σ is independent of T. The value of σ depends on the mean distance of approach of the molecules on impact. This depends on the repulsive forces between molecules and their energy of agitation. The greater the forces the greater the apparent value of σ. Since increased T means an increase in kinetic energy, and hence a lessened effect of attractive forces on the free paths of the molecules, as well as a closer approach on impact, it is not surprising that η is found to increase more rapidly with T than the $\sqrt{T}$. If η were found proportional to T, then σ would only have to vary as $\frac{1}{\sqrt[4]{T}}$ to cause this. This is not a very rapid change. It seems, however, worth while to point out that the deviation is not serious from the point of view of the establishment of the kinetic theory, for it predicts an increase in η with T which is nearly fulfilled, whereas previous experience with liquids showed the reverse effect. The deviation is, however, very welcome, as it makes it possible to test the variation of σ, the apparent diameter, with T and thus leads to an evaluation of intermolecular forces. This will be discussed more at length in Sec. 62, under the theory of Sutherland.

The measurements of η afford the best values of L obtainable. Thus a check of the theory from the point of view of a prediction of the value of η from theory and a comparison with the observed values is meaningless, for L otherwise determined is far less exact. It is interesting to compute η at 0°, 760, for N_2 from σ derived

from Van der Waals' b and compare it with the observed value. For air, $\sigma = 3.53 \times 10^{-8}$ cm,

$$m = 28.0 \times 1.66 \times 10^{-24} \text{ grams } \bar{c} = 4.54 \times 10^{4} \text{ cm/sec.}$$

$$\eta = \frac{28.0 \times 1.66 \times 10^{-24} \times 4.54 \times 10^{4}}{3\sqrt{2}\,\pi\, 1.245 \times 10^{-15}}$$

$$\eta = 1.27 \times 10^{-4}$$

The value of η observed for N_2 at 0° is

$$\eta = 1.66 \times 10^{-4}.$$

The values agree in order of magnitude but differ by about 17 per cent. Part of this discrepancy would be taken care of by the Tait free path. If a constant in the equation computed by Jeans,[1] including a correction for what he terms the "persistence of velocities," were used, a very good agreement would result in this case. It is seen, therefore, that, while the result is approximately correct, the question of the constant factor is an important one. Again, it must be pointed out that it is questionable to *use values of σ obtained from critical data with those from viscosity theory*, for the real significance of a value σ depends on the measurements from which it is deduced. Thus it is quite probable that the value of σ entering into b is not the same as the one used for viscosity.

61. Criticisms of the Simple Theories.—In what has preceded, certain points were passed over as sufficiently accurate, with little or no comment. Two of these merit further discussion and will be taken up in this section.

The first limitation for the development is that it postulates that the state of motion is nearly steady, *i.e.*, that the speed of the gas stream at any point does not vary much with the time. This requirement is introduced by the fact that no distinction is made between the time at which the molecules leave the volume element dv and the time at which they cross the surface element $dxdy$. The numerical magnitude of this limitation will be estimated later.

A second point bears on the validity of the assumption that "on the average, a molecule possesses the x-component of momentum appropriate to the scene of the last collision." The analysis of this assumption and associated ones occurring in the theory of heat conduction and diffusion and have been treated by Jeans[1] under the designation of "persistence of velocities." The analysis pertaining to this correction is given in his "Dynamical Theory of Gases," and only the results will be given in this text.

Passing now to the more detailed study of the first of these corrections, it is important to determine *the thickness of the gas layer in which practically all of the viscous action takes place.* In the theory of Maxwell the momentum transfer is integrated over all space. Actually, however, the distant volume elements contribute practically nothing to the viscous action across $dxdy$. The expression for η after integration over the polar angles θ and ϕ is

$$\eta = \frac{1}{3} Nm \frac{\bar{c}}{L} \int_0^\infty e^{-\frac{r}{L}} r\,dr = \frac{1}{3} Nm\bar{c}L.$$

If one considers the viscous action of those molecules whose last collision occurred at a place less than d distant from the place of crossing $dxdy$, this will be less than the total amount by the following fraction of the total viscous action:

$$\int_d^\infty e^{-\frac{r}{L}} \frac{r\,dr}{L^2} = e^{-\frac{d}{L}}\left(\frac{d}{L} + 1\right).$$

This shows that all but about 4 per cent of the viscous action across a surface is effected by the crossing of molecules within a distance of five times the mean free path from the place of crossing, while all but 0.3 per cent is gained by including molecules from distances up to eight times the free path. The conclusion is that virtually all of the viscous action in a gas occurs over an extremely thin layer of the gas.

The result of the preceding analysis makes it possible to form an estimate of the amount of the error made in neglecting the distinction between time of leaving dv and time of crossing $dxdy$ Molecules coming from a greater distance than $8L$ need not be considered and the time for the average molecule to go this distance is given by $\frac{8L}{\bar{c}}$, a quantity whose order of magnitude is 10^{-9} sec. Thus the deviations from the steady state occurring in practice are unimportant in their effect on the theory. This is especially true, since modern methods utilize only the steady state.

62. Sutherland's Theory.[5]—To clear up the discrepancy which arose when it was found that the experimental increase of η with temperature was greater than that indicated by the simple considerations just presented, Sutherland gave a simple analysis of the effect of attractive forces between the molecules.

If the molecules are hard elastic spheres whose centers attract each other according to some law of the distance, there are two ways in which exchanges of momentum may occur:

1. The molecules may pass near each other so closely that one affects the other without an actual collision, or

2. They may collide with each other in the same manner as "forceless" elastic spheres.

The Sutherland[5] theory ignores the effect of the first mode of exchange of momentum on the viscosity and considers how the action of attractive forces may serve to increase the number of collisions. Since the mean free path is altered as well by the first as by the second type of collisions, the theory can hardly be thought of as being adequate until this is done.

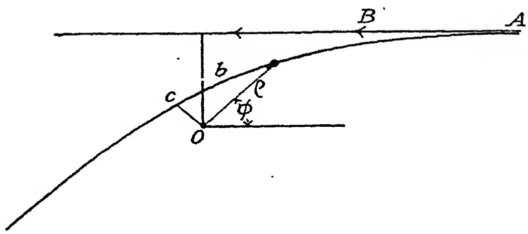

FIG. 34.

It is sufficient to consider the motion of one molecule relative to the other. In the Fig. 34 let O be the center of one molecule and let $\overrightarrow{AB}$ be the direction of the motion of the other molecule relative to O. The curved line represents the actual orbit of the moving molecule, C the point of minimum approach, b the distance which would have been that of minimum approach if no forces acted, ρ and ϕ polar coordinates of center of the moving molecule.

Let $mF(\rho)$ be the magnitude of the force between the molecules when their distance apart is ρ; then the equations of motion* are[6]

$$\frac{d^2x}{dt^2} = -F(\rho)\,\frac{x}{\rho};\ \frac{d^2y}{dt^2} = -F(\rho)\,\frac{y}{\rho}.$$

These may be combined in the usual way to obtain the integral of angular momentum in polar coordinates:

$$\rho^2\frac{d\phi}{dt} = h,\ \ i.e.,\ \ \frac{d\phi}{dt} = \frac{h}{\rho^2}.$$

* The treatment here is based on the standard case of the two-body problem with central forces in one plane. The law of force is undefined. The treatment may easily be found in such texts in dynamics as Routh, or Webster, under the title Dynamics of a Particle.

If they are combined to form the energy integral, then:

$$\frac{d(r^2)}{dt} = -2F(\rho)\frac{d\rho}{dt},$$

in which r^2 is the square of the relative speed,

$$r^2 = \left(\frac{d\rho}{dt}\right)^2 + \rho^2\left(\frac{d\phi}{dt}\right)^2 = \left(\frac{d\rho}{dt}\right)^2 + \frac{h^2}{\rho^2}.$$

On differentiating this latter relation,

$$2\frac{d\rho}{dt}\cdot\frac{d^2\rho}{dt^2} - 2\frac{h^2}{\rho^3}\frac{d\rho}{dt} = -2F(\rho)\frac{d\rho}{dt}$$

or

$$\frac{d^2\rho}{dt^2} - \frac{h^2}{\rho^3} = -F(\rho).$$

To obtain the value of h it is observed that when the molecules are separated to great distances

$$h = rb,$$

where r is the relative velocity. Integrating the differential equation and determining the constant by the fact that $\frac{d\rho}{dt} = r$ when $\rho = \infty$,

$$r^2 - \left(\frac{d\rho}{dt}\right)^2 = \frac{b^2r^2}{\rho^2} - 2\int_\rho^\infty F(\rho)d\rho.$$

At the position of minimum approach CO, $\rho = \rho_0$ and $\frac{d\rho}{dt} = 0$. For this distance the preceding equation yields:

$$r^2 - \frac{b^2r^2}{\rho_0^2} + 2\int_{\rho_0}^\infty F(\rho)d\rho = 0$$

or

$$b^2 = \rho_0^2\left[1 + \frac{2}{r^2}\int_{\rho_0}^\infty F(\rho)d\rho\right].$$

Now collisions will occur if ρ_0 is equal to σ or smaller, so the preceding equation shows that the effect of the attracting force is to make the effective sphere of action, of radius b, greater than σ, that of the forceless spheres. This enters into the free-path considerations of Sec. 37 in such a way as to substitute b^2 for σ^2 and thus gives the new free-path formula:

$$L_s = \frac{1}{\sqrt{2}\pi N\sigma^2\left[1 + \frac{2}{r^2}\int_\sigma^\infty F(\rho)d\rho\right]},$$

where L_s designates the Sutherland modification of the Maxwell free path. Since r^2 is proportional to the absolute temperature,

$$\frac{2}{r^2}\int_\sigma^\infty F(\rho)d\rho = \frac{D}{T},$$

where D is a constant characteristic of each gas. The free path then becomes such a function of the temperature as is given by

$$L_s = \frac{L_m}{1 + \frac{D}{T}},$$

where L_m is the Maxwell free path of Sec. 37.

If this value be substituted in the Tait viscosity expression of Sec. 59 one obtains:

$$\eta = \frac{1}{3} Nm\bar{c} \frac{1.051 L_m}{1 + \frac{D}{T}}.$$

Reinganum[7] has used the same physical picture—that of attracting rigid elastic molecules—and by other mathematical methods has obtained for the temperature variation of η the formula

$$\eta \propto T \cdot e^{-\frac{D'}{T}},$$

in which D' is a constant characteristic of each gas, analogous to the Sutherland constant. The derivation results from the use of the theorem of the virial and proceeds along lines similar to that of his equation of state (Sec. 54).

63. Measurement of Viscosity.—Before proceeding to more detailed discussion of experimental results it is desirable to discuss briefly the methods of measuring viscosity. The oldest method is based on the study of the rate of flow of the fluid through a capillary tube. The flow of liquids through capillaries was first studied systematically by Jean Louis Marie Poisseuille,[8] a French anatomist, who was interested in the physics of the circulation of the blood. His work was published in 1842. Other methods are based on the measurement of the damping of the oscillations of pendula,[9] the constant deflecting force of a cylinder in a rotating gas,[10] the fall of small spheres through a gas,[11] etc.

The foundation of all the methods lies in the solution of the hydrodynamical problem of fluid motion corresponding to the arrangement used. The theory of some of the methods is simple, while others lead to difficult problems in partial differential equations. The student who is interested in the hydrodynamic side of viscous fluid flow is referred to Lamb's[12] "Hydrodynamics."

In deriving the Poisseuille's empirical formula from hydrodynamics it is assumed that all motion of the fluid is parallel to

the length of the tube. This requires that the tube be very long compared to its diameter in order that irregular end effects be negligible. At the wall of the tube the fluid slips, so that the difference in speed between the wall and the fluid adjacent to it is

$$v = \frac{\eta}{\epsilon}\frac{\partial u}{\partial z},$$

in which ϵ is the "coefficient of external friction" (see Chap. VII, Sec. 77). The solution of the appropriate differential equations then yields for the volume of fluid flowing through the tube in unit time (Sec. 77)

$$V = \frac{\pi P}{8\eta L}\left(R^4 + \frac{4\eta}{\epsilon}R^3\right),$$

in which P is the pressure difference between the two ends, L is the length of the tube, and R is its radius. If there is no slipping of the gas along the walls, $\epsilon = \infty$ and the formula is

$$V = \frac{\pi P R^4}{8\eta L}.$$

Graetz[13] gives the corresponding solutions for capillaries of other forms than circular cross-section. Osborne Reynolds[14] has shown that above the critical velocity

$$v = \frac{2000\eta}{2R\rho},$$

in which ρ is the density of the fluid, the motion becomes turbulent, and Poisseuille's law fails. Most of the research work on gas viscosity has been carried out by the study of the flow of gas in capillary tubes.

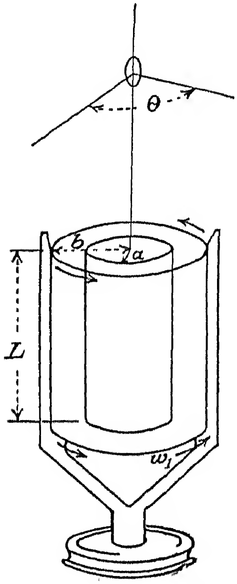

Fig. 35.—Rotating cylinder method for measuring viscosity of gases.

A method, capable of high precision, which has probably given the best recent results, is that of the constant deflection of a cylinder in a rotating mass of gas. This is described by Gilchrist[15] and by E. R. Harrington.[16]

In this method a cylinder (Fig. 35) is hung up by a delicate suspension so that it may turn about a vertical axis. Surrounding the cylinder is a larger one which is rotated at a uniform speed. The gas is set in motion and the viscous forces which act on the inner cylinder cause it to turn until these forces are balanced by the torsional action of the twisted suspension. Let it be supposed that the radius of the inner cylinder is a and that of the

outer cylinder is b, while the angular velocity of the outer cylinder is w_1. Let L be the length of the cylinders. In the steady state the speed of the gas will be zero at the inner cylinder and bw_1 at the outer cylinder. The force on an imaginary cylinder of radius r in the gas will be

$$F = 2\pi rL\eta\frac{\partial v}{\partial x}$$

and the moment of this force is

$$\overline{Fr} = 2\pi r^2L\eta\frac{\partial v}{\partial r}.$$

By $\frac{\partial v}{\partial r}$ is to be understood the rate of change of the relative motion of adjacent layers of the liquid. To find this one may write

$$v = rw,$$

then

$$\frac{\partial v}{\partial r} = w + r\frac{\partial w}{\partial r}.$$

However, the w on the right-hand side arises from the variation in v which would be present if the gas rotated with uniform angular velocity, like a rigid body, when certainly no viscous action is developed. This term therefore does not enter into the value of $\frac{\partial v}{\partial r}$ to be used in the analysis. As a measure of the rate of shear of the gas one then has $\frac{\partial v}{\partial r} = r\frac{\partial w}{\partial r}$, and hence

$$\overline{Fr} = 2\pi r^3\eta L\frac{\partial w}{\partial r}$$

gives the torque which each outer gas layer exerts on the adjacent one inside. In the steady state the torque exerted by each layer must balance the reaction of that which each adjacent layer exerts, since the angular acceleration of the gas is zero, that is, $\overline{Fr}$ is constant throughout the gas. The preceding equation may be now integrated as follows:

$$\overline{Fr}\int_a^b\frac{dr}{r^3} = 2\pi\eta L\int_0^{w_1}dw$$

$$\overline{Fr}\left[\frac{1}{a^2} - \frac{1}{b^2}\right] = 4\pi\eta Lw_1$$

or

$$\overline{Fr} = 4\pi\eta L\frac{a^2b^2}{b^2 - a^2}w_1.$$

The torque $\overline{Fr}$ is that exerted on the inner cylinder. It is measured by the angle of deflection of the inner cylinder, the amount of torque for a given angle of deflection being first determined by independent experiments, that is to say, $\overline{Fr} = T_0\theta$, where T_0, the torsional constant of the fiber, may be found from the period of oscillation of the cylinder.

64. Experimental Results.—The simple theory of viscosity predicts that η should be independent of the density. At low pressures, this breaks down because the free path becomes comparable

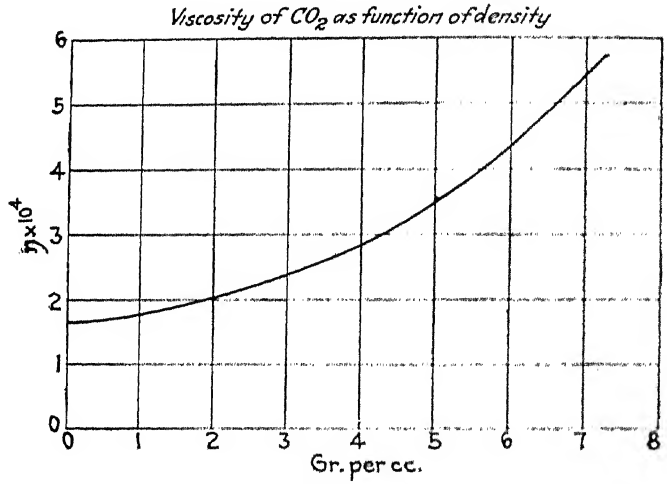

FIG. 36.

with the size of the vessel (Chap. VII). At very high pressures, deviations will result from the increasing effectiveness of the forces between the molecules. All experimenters find η accurately independent of density[3] from 760- down to 10-mm pressure. Below this pressure surface phenomena intervene.

Warburg and Babo[17] have carried out an interesting set of measurements of η for carbon dioxide at high pressures. The theory predicts that η should be independent of density; independence of pressure then follows if the perfect gas laws are applicable. These are not applicable for CO_2 at high pressures, and so it is more significant to discuss the relation between η and density. Figure 36 shows a plot of the Warburg and Babo measurements of η as ordinates against the density as abscissæ. An indication of the extent of the deviation from perfect gas

conditions is given by the fact that a pressure of 45.3 atmospheres made the density 0.1, which is about 500 times the density for 1 atmosphere.*

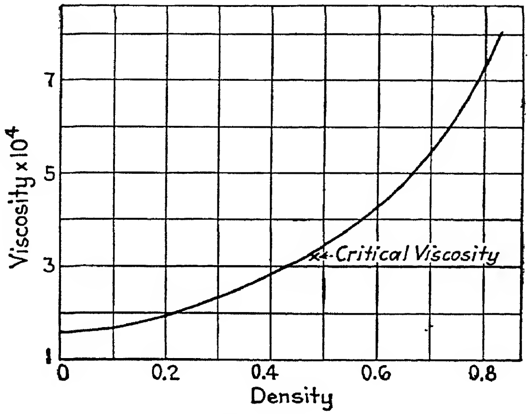

FIG. 37.

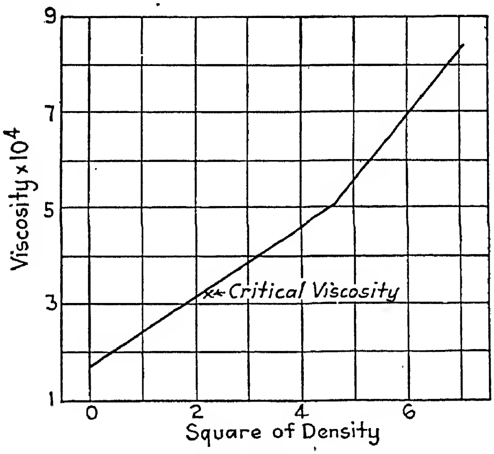

FIG. 38.

* Recently, P. Phillips[18] (*Proc. Roy. Soc.*, **A87**, 48, 1912) has made a more extended study of the variation of the viscosity of carbon dioxide with pressure. His measurements extend to 120 atmospheres' pressure at temperatures 20, 30, 32, 35, and 40° and thus extend into the liquid state through the critical point. Figure 37 from Phillips' paper shows the variation of η with pressure at one temperature. Figure 38, also from Phillips, shows η plotted against the square of the density, indicating that the relation of η to density, while parabolic, has an abrupt change of parameter at about $d^2 = 0.48$.

This relationship, Phillips points out, "would mean that in this region of very rapid alteration of density with temperature or pressure the change

The curves show that the viscosity is remarkably independent of the density even in a region where large deviations from the gas laws have set in. As the density is increased still further, the molecular forces provide an increment to the viscosity which is approximately proportional to the square of the density.

Turning now to the variation of η with temperature, experiment shows that the Sutherland formula (Sec. 63) fits the facts over the range of conditions in which it could be expected to be valid. Bestelmeyer[19] was the first to make measurements suitable for testing the formula over a wide range of temperatures. He found for nitrogen the following ratios of η_t to $\eta_{17°}$, the viscosity at 17°C.:

t	300.4	98.41	−78.66	−190.63
$\frac{\eta_t}{\eta_{17}}$	1.6279	1.2064	0.7204	0.3204

and showed that the deviations of these measures from the Sutherland formula with $D = 110.6$ were less than 3 per cent. Similarly, Markowski[20] checked the Sutherland formula for hydrogen, oxygen, and nitrogen between 0 and 180°C., as did Schmidt[21] from −195 to +185°C. on air, helium, hydrogen, argon, nitrogen, and oxygen. On the other hand, Zimmer finds the Sutherland formula incorrect below −20°C. for ethylene and carbon monoxide, the actual viscosity being greater than the formula would indicate. The deviation is discussed in connection with a hypothesis of association of the gas molecules. K. Onnes[23] finds the Sutherland formula inadequate for hydrogen and helium at very low temperatures. Probably the best treatment of viscosity given is that of Chapman,[27] whose general treatment of transfer theory gives the best theoretical results obtained. His work, which is beyond the scope of this book, will be discussed more in Parts II and III of this chapter.

65. Relation of Viscosity to Molecular Constitution.—In recent years, A. O. Rankine[24] and associated investigators have obtained some interesting results connecting viscosity, and hence molecular size, with chemical constitution. The investigations were carried out by means of an ingenious modification of the

in viscosity is due almost entirely to the change in attraction between two adjacent layers of the fluid, for this would be proportional to the square of the density. In other words, the viscosity in this region depends almost entirely on the $\frac{a}{v^2}$ term in the Van der Waals' equation."

capillary-flow method. The Sutherland formula is assumed as valid. The constant D was determined from measurements of η at two different temperatures.

The work on the inert gases gives values for the relative atomic diameters, which are plotted in Fig. 39 against the atomic number of these elements. These results indicate that there is a break in the rate of increase in size of the atoms at argon, where there is an abrupt change in slope of the line joining the points. It is to be noted that this is the point in the periodic table where the first long period begins and shells containing many electrons begin to be added. C. J. Smith[25] compared the values of η for

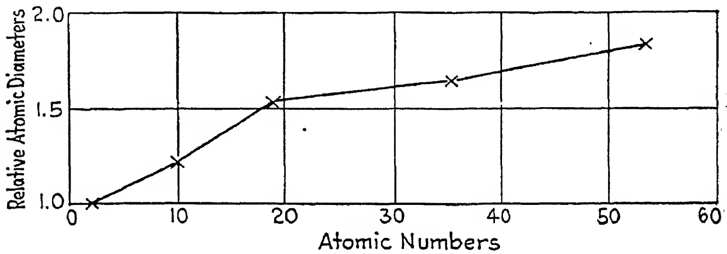

FIG. 39.

CO_2 and N_2O, also CO and N_2. It will be noticed that the gases in both pairs have the same molecular weights. He found

Temperature, degrees centigrade	$\frac{\eta CO_2}{\eta N_2O}$	$\frac{\eta CO}{\eta N_2}$
15.0	1.001	1.000
100.0	1.003	1.001

indicating that these similar molecules of similar weight have practically the same size and free paths.

Rankine and Smith[26] have also carried out an interesting study designed to show the change in collision area of a series of molecules whose weights were the same but which contained an increasing number of hydrogen atoms. The gases chosen, and the ratios of their collision area found, are:

Ar	1.00	PH_3	1.41
HCl	1.04	SiH_4	1.53
H_2S	1.19		

Assuming the Sutherland formula for extrapolation, Rankine[11] has computed the viscosities of the rare gases at their critical temperatures and has found the values to be proportional to the square root of the atomic weight. He has further noticed that the ratio of the critical temperature to the Sutherland constant D is a constant for several gases examined, the mean value being

$$\frac{T_c}{D} = 1.14.$$

Hydrogen is an exception, the ratio being 0.45 for this gas.

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II. HEAT CONDUCTION

66. Definition of Heat Conduction.—In Sec. 56, the transfer of heat in a gas by the molecules of the medium ~~was~~ can be shown to occur in two ways. The first mechanism depends on the effect of the earth's gravitational field on the changes in density produced by the temperature gradients, and was termed "convection." It is the result of mass motion of the gas, and consequently is not directly a kinetic phenomenon. A treatment of such mode of transfer falls primarily into the domain of hydrodynamics. The second mode of transfer operates in all cases of gaseous heat conduction and it constitutes an essential phase of the exchange of heat between the layers of different temperatures set up by convection. (As was stated) it depends on the direct transfer of kinetic energy by molecules of one layer with a higher energy to molecules of lower average energy in another layer. Thus it is a strictly molecular phenomenon and may be treated by the kinetic theory.

As the gravitational field of the earth is ever present, it becomes practically very difficult to avoid the occurrence of convection in the experimental study of conduction. By the proper choice of orientation of the plates in the gravitational field (*e.g.*, placing them normal to the earth's field, the hotter one above), by use of low gas pressures, and by the use of very narrow gaseous gaps the convection may be relegated to a relatively insignificant place in the heat transfer between the surfaces considered.

If two large horizontal planes are assumed, the upper one at a temperature T, the lower one at a temperature T_0 separated a distance d, the quantity of heat Q transferred from one plate to the other across an area A in a time t is given by

$$Q = KA(T_1 - T_0)f(d)t,$$

where $f(d)$ stands for some function of d. As the distance d is decreased, the equation takes on the form

$$Q = KA\frac{T_1 - T_0}{d}t.$$

This is precisely the relation found for the case of unidirectional flow of heat through a large plane of solid substance by conduction. The occurrence of this equation indicates that all convection has ceased and that one may consider K, the constant of proportionality, to have the same meaning as that given for solids. Experiment shows that it is a constant for each kind of gas. Thus when convection is eliminated in a gas, heat transfer follows the same laws as for solids, the gas having a constant for heat conductivity characteristic of itself. The constant depends on the speed with which molecules of a higher energy content can diffuse into regions of lower energy content through the gas, that is, it is really a function of the rate of molecular transfer of kinetic energy from layer to layer. In solids, the conduction of heat[3] seems to be an entirely different phenomenon, although the mechanism is little understood. In these bodies the molecules are rigidly bound in equilibrium positions by elastic forces. Their heat motions are then oscillations about their positions of equilibrium. To what extent heat conductivity depends on the transfer of energy from one quasi-elastically bound molecule to its nearest neighbor is little known. The close ratio of electrical conductivity of metals to their heat conductivity, evidenced by the Wiedemann-Franz[1] law, has suggested a more kinetic picture of this conduction. It seems possible that there exist, in the metals at least, free electrons in some numbers, darting here and there through the regular channels between the evenly spaced molecules. Such electrons were supposed to lead to the thermionic emission[2] and the electrical conductivity. On the basis of the Wiedemann-Franz law, it may be possible that they are also instrumental in the heat conductivity. If this were so, the mechanism in some solids could be considered similar in nature to gaseous conduction. On the whole, it is probably safer to assume that the elastic vibrations play the predominating rôle. Thus, although gaseous conduction obeys the same law as conduction in solids, it probably is due to an entirely different mechanism. It is not surprising, therefore, that the K for gases increases as T increases, while the similar quantity for metals decreases.

It is more accurate to write $\frac{T_1 - T_0}{d}$ in the differential form denoting d as dz, an element of distance chosen along the z-axis normal to the plates. It must be remembered, in representing $\frac{T_1 - T_0}{d}$ by $\frac{dT}{dz}$, that the flow always takes place from the hotter to the colder point. The magnitudes of heat conductivity K for various types of conductors are given below to familiarize the reader with the magnitudes involved. K in the c.g.s. system gives the calories carried across 1 cm^2 in a second when there is a temperature gradient of 1°C. per cm normal to the plates.

TYPICAL VALUES OF K

Gas or substance	Temperature, degrees centigrade	K
Air	0	0.0000568
He	0	0.000339
H_2O (liquid)	0	0.00143
Paper	..	0.0003
Brick	..	0.0015
Al	18	0.504
Cu	13	1.00
Ag	18	1.00

67. The Simple Kinetic Theory of Heat Conduction.—The considerations involved in the evaluation of K are quite analogous to those involved in the evaluation of η as given in Sec. 58. With K, however, it is not momentum that is transferred, but kinetic energy. With this difference the two simple deductions are essentially parallel.

Assume the gas arranged in layers normal to the z-axis, the warmer layers being uppermost. Then T depends on z only. When the steady state is reached, as much heat flows out of any layer at a given time as flows into it, that is, from the equation of continuity[4] for this case, $\frac{d^2T}{dz^2} = 0$, and integration leads to an equation which states that $\left(\frac{dT}{dz}\right)$ is a constant. Hence at any point of the gas $T = T_0 + \frac{dT}{dz}z$, where $\frac{dT}{dz}$ is positive in the

arrangement under consideration. One-third of all the molecules are moving along the z-axis, or one-third of all the velocity components lie along z. These are the molecules which carry heat from one layer to the other. If the mean free path be L, one may, as before, consider a layer of thickness L. The average temperature difference of the molecules on the two sides of this layer will then be $L\frac{dT}{dz}$. If each molecule has a mass m and the specific heat of the gas is $= C_v$,* the difference in energy content of the molecules is $mC_vL\frac{dT}{dz}$. Of the third of the molecules moving along z, one-half are moving downward. In 1 second $\frac{1}{6}N\bar{c}$ molecules pass downwards through each cm² of the layer L and carry energy which is equal to $\frac{1}{6}N\bar{c}mC_vL\frac{dT}{dz}$ downwards. Here N is the number of molecules per cm³ and $\bar{c}$ is the average velocity. Likewise, $\frac{1}{6}N\bar{c}$ molecules pass upward and they carry $-\frac{1}{6}N\bar{c}mC_vL\frac{dT}{dz}$ in energy units upwards across 1 cm² in unit time. The negative sign comes in here, as the gradient below the T_0 plane is negative. The total energy transfer is the difference of the energy carried down and that carried up. Taking this difference, one has $\frac{Q}{At}$ the energy carried per cm² per second as

$$\frac{Q}{At} = \frac{1}{3}N\bar{c}mC_vL\frac{dT}{dz}.$$

But by definition $\frac{Q}{At} = K\frac{dT}{dz}$.

Hence $$K = \frac{1}{3}Nm\bar{c}LC_v.$$

Since, however, $\eta = \frac{1}{3}Nm\bar{c}L$, one has the interesting relation,

$$K = \eta C_v.$$

This equation is also the one obtained from the more complete derivation which takes into account the distribution of velocities

* This would be strictly true for a monatomic gas where there is only energy of translation in C_v. It seems that where rotational energy is concerned the contribution to this in C_v might be expected to be involved in the energy transfer to its full value. This does not seem to be true, as will be seen in Sec. 69.

as well as the distribution of free paths. Neither of these deductions are strictly rigorous and a discussion of the values of K will follow at the end of Sec. 69, where a more rigorous treatment is outlined. The elementary reader would do well to read the introduction to Sec. 69 and, omitting the mathematics, read the discussion at the end of the section. In the next section the more complete deduction, taking into account the distribution of free paths and velocities, will be given.

68. Deduction of the Constant of Heat Conduction, Taking into Account the Distribution of Free Paths and Velocities.—To derive the expression for the transfer of energy from one layer of the

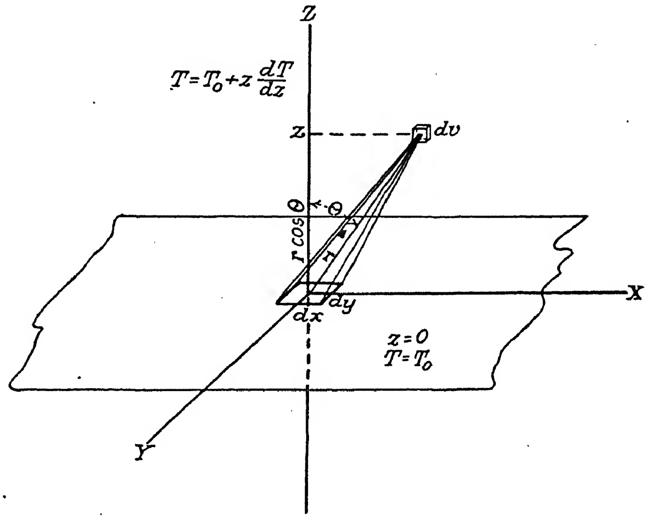

FIG. 40.

gas to the other by the molecules, one may proceed as follows: Assume a gas space large in extent having a uniform temperature gradient, the temperature above being higher than that below. Assume that the steady state has been reached and consider the transfer of heat across the xy plane taken normal to the temperature gradient along the z-axis. At the xy plane assume the temperature to be T_0. Thus above xy the temperatures will be $T = T_0 + z\frac{dT}{dz}$ and below this plane the temperatures will be $T = T_0 - z\frac{dT}{dz}$. To start with, attention may be concentrated upon a small area $dxdy$ of the xy plane (Fig. 40) and the total

number of molecules crossing this in unit time from above and below considered. The net energy transfer due to these molecules will give the total heat conduction and hence determine K. Consider a small volume dv at r cm from $dxdy$ such that the line r connecting dv and $dxdy$ makes an angle θ with the normal to $dxdy$, *i.e.*, with the z-axis. Thus z for the volume dv is $r\cos\theta$. If each of the molecules in dv has a mean free path L and a velocity c, then each molecule starts a *new free path* $\frac{c}{L}$ times a second. Now in dv there are $Ndv\frac{4}{\alpha^3\sqrt{\pi}}c^2e^{-\frac{c^2}{\alpha^2}}dc$ molecules having a velocity between c and $c + dc$, where N is the number of molecules in a cm^3. Hence $\frac{4N}{\alpha^3\sqrt{\pi}}\frac{c}{L}dvc^2e^{-\frac{c^2}{\alpha^2}}dc$ molecules of speed c will leave dv in a second (see Sec. 35). Of these, the number in a cone of base $dxdy\cos\theta$ will have paths directed towards θ if all directions are equally probable. That is, $\frac{dxdy\cos\theta}{4\pi r^2}\frac{4}{\alpha^3}\frac{N}{\sqrt{\pi}}\frac{c^3}{L}dve^{-\frac{c^2}{\alpha^2}}dc$ particles will leave dv per second headed for $dxdy$ along r. Of these, the fraction $e^{-\frac{r}{L}}$ (see Sec. 21) only will succeed in crossing $dxdy$ without impact. As each of these is assumed to have an energy corresponding to the position of dv in the region in which heat is being transferred, its temperature will be

$$T_z = T_o + z\frac{dT}{dz}.$$

Each molecule that leaves dv will then carry an amount of energy

$$mC_v\left(T_o + z\frac{dT}{dz}\right)$$

from dv through $dxdy$, where m is the mass of a molecule and C_v is the specific heat. Thus the energy carried from dv in a time dt through $dxdy$ by the molecules of all speeds is

$$dE = \frac{-Ndxdy\cos\theta dvdtmC_v}{4\pi r^2L}e^{-\frac{r}{L}}$$

$$\left(T_o + r\cos\theta\frac{dT}{dz}\right)\frac{4}{\alpha^3\sqrt{\pi}}\int_0^\infty c^3e^{-\frac{c^2}{\alpha^2}}dc$$

$$= -NdxdydtdvmC_v\frac{\bar{c}}{L}\left[\frac{T_0e^{-\frac{r}{L}}\cos\theta}{4\pi r^2} + \frac{\cos^2\theta\frac{dT}{dz}e^{-\frac{r}{L}}}{4\pi r}\right]$$

where the evaluation of $\int_0^\infty \frac{4}{\alpha^3\sqrt{\pi}} c^3 e^{-\frac{c^2}{\alpha^2}} dc$ gives the quantity $\bar{c}$. Since $dv = (rd\theta)\ (r \sin \theta d\phi)\ dr$, the total energy transferred from the whole hemisphere is the integral of dr from 0 to infinity, of $d\theta$ from 0 to $\frac{\pi}{2}$, and of $d\phi$ from 0 to 2π. Hence the amount of energy transferred from above the xy plane downward in the time dt is $\frac{dQ}{dt}\downarrow$.

$$\frac{dQ}{dt}\downarrow = \frac{-N\bar{c}dxdymC_v}{L}\left[\frac{T_0}{4\pi}\int_0^\infty e^{-\frac{r}{L}}dr \int_0^{\frac{\pi}{2}} \cos\theta \sin\theta d\theta \int_0^{2\pi} d\phi \right.$$
$$\left. + \frac{1}{4\pi}\frac{dT}{dz}\int_0^\infty re^{-\frac{r}{L}}dr \int_0^{\frac{\pi}{2}} \cos^2\theta \sin\theta d\theta \int_0^{2\pi} d\phi \right].$$

In a similar fashion the energy transferred from below the xy plane upward amounts to

$$\frac{dQ}{dt}\uparrow = \frac{+Ndxdy\,\bar{c}mC_v}{L}\left[\frac{T_o}{4\pi}\int_0^\infty e^{-\frac{r}{L}}dr \int_0^{\frac{\pi}{2}} \cos\theta \sin\theta d\theta \int_0^{2\pi} d\phi \right.$$
$$\left. - \frac{1}{4\pi}\frac{dT}{dz}\int_0^\infty re^{-\frac{r}{L}}dr \int_0^{\frac{\pi}{2}} \cos^2\theta \sin\theta d\theta \int_0^{2\pi} d\phi \right].$$

The $-$ sign in the $\frac{dQ}{dt}\downarrow$ indicates that the heat goes from a lower to a higher temperature, and the $-$ sign in the brackets in $\frac{dQ}{dt}\uparrow$ comes from the fact that below the xy plane the temperature at any point r cm away from $dxdy$ is $T_0 - r\cos\theta\frac{dT}{dz}$. Adding the two terms and integrating, the net energy transfer is

$$\frac{dQ}{dt} = -\frac{1}{3}Nm\bar{c}LC_v dxdy\,\frac{dT}{dz}.$$

But K is defined as

$$\frac{dQ}{dt} = -Kdxdy\,\frac{dT}{dz}.$$

Hence $K = \frac{1}{3}Nm\bar{c}LC_v = \eta C_v$, as was found before.

69. Correction of the Derivation of the Coefficient of Heat Conductivity and Comparison with Experiment.—The preceding

derivation, strictly speaking, was not rigorous, although it is experimentally valid in order of magnitude. The error lies in two effects. In the first place, since the pressure is constant (*i.e.*, since there is no mass motion in the gas), while T varies from place to place, the density of the gas must be variable and decreases as T increases. This means that N varies with z in such a fashion that $N = N_o - z\frac{dN}{dz}$ above the xy plane and $N = N_o + z\frac{dN}{dz}$ below this plane. In the second place, c varies with T and hence the collision frequency Ξ and the free path which depends on it $\frac{c}{\Xi}$ are both functions of z. These were neglected in the previous derivation. This requires the use of the velocity free path and collision number in place of the terms $\frac{c}{L}$, and L, in the equations above. Finally, it was assumed that the Maxwell distribution law held in this derivation. Since this law is an equilibrium law, it cannot hold here, for heat conduction is *not an equilibrium phenomenon* (see Sec. 56). This error is probably slight because the lack of equilibrium due to the small differences of velocities involved in heat conduction is small when compared to the velocities existing among molecules in thermal equilibrium. It will therefore be overlooked in what follows. This neglect may in part be responsible for the discrepancies observed in the more rigorous equation to be discussed. It might be added in passing that the simple equation deduced above seems to fit as well as it does in view of these omissions since conduction takes place over short distances, so that the changes in N with r are comparatively small, and thus the errors introduced are not serious.

The question of these corrections has been attacked from the point of view of this text by many workers. O. E. Meyer[5] and Jeans[6] have given the treatments which most closely reproduce the true state of affairs and are generally accepted. The treatment of Jeans follows the plan laid out by Meyer, however, adding some corrections. Chapman[7] and Enskog,[8] using a different line of reasoning, have carried out a more accurate study applicable to monatomic gases and depending on the law of force assumed between the molecules. These treatments are, in the main, beyond the scope of this book, and for complete details

the reader is referred to the original articles. It seems, however, instructive to note the way in which Meyer[5] introduces the corrections into this equation and to point out wherein Jeans extends them. This will be done briefly in what follows.

Let each molecule leaving the volume dv considered above carry with it the energy $\frac{1}{2}mc^2$ appropriate to the average molecular energy in dv. In this volume the mean collision frequency must now be represented by the factor Ξ in place of $\frac{c}{L}$ and the mean free path under these conditions will be represented by $\frac{c}{\Xi}$. An analysis similar to that of Sec. 68 then leads to the expression for the energy transferred per second through $dxdy$ from a volume dv above the xy plane as expressed by

$$\frac{dQ}{dt} = \frac{mc^2}{2}\frac{dxdy\cos\theta}{4\pi r^2}r^2\sin\theta d\theta d\phi dr\Xi e^{-\frac{\Xi r}{c}}\frac{4N}{\alpha^3\sqrt{\pi}}c^2e^{-\frac{c^2}{\alpha^2}}dc.$$

At this point in the analysis it is convenient to replace the α of the distribution law by the factor $\frac{1}{\sqrt{hm}}$ to conform to the equations used by Meyer and Jeans in order to facilitate comparison with these writers. This transformation is carried out in another portion of the text (Sec. 43). For convenience, it will be repeated in a footnote.* Collecting the terms and making the substitution, the total heat transfer from one side of the xy plane to the other through $dxdy$ after carrying out the proper integrations, may be represented as,

$$Q = \frac{1}{2}m\int_0^{2\pi}d\phi\int_0^{\frac{\pi}{2}}dxdy\sin\theta\cos\theta d\theta$$
$$\int_0^\infty N\left(\frac{hm}{\pi}\right)^{3/2}dr\int_0^\infty c^4\Xi e^{-\Xi\frac{r}{c}}e^{-hmc^2}dc.$$

The integrations to be performed are complicated by the added

* $\frac{1}{3}NmC^2 = RT$. Calling $\frac{R}{N} = k$, the Boltzmann constant, one has $C^2 = \frac{3kT}{m}$. As $\alpha^2 = \frac{2}{3}C^2$ (Sec. 35), one may write $\alpha^2 = \frac{2kT}{m}$. If $h = \frac{1}{2kT}$, α becomes $\frac{1}{\sqrt{hm}}$.

facts that $N = N_o \mp \frac{dN}{dz} r \cos\theta$, and that $h = h_o \pm \frac{dh}{dz} r \cos\theta$, the plus and minus signs referring to the regions above and below the xy plane, where $N = N_o$ and $h = h_o$. Since r is a small quantity, terms involving higher powers may be neglected and a substitution of these values for N and h makes the equation for the total energy transfer through $dxdy$ take the following form:

$$Q = \frac{1}{2} Nm\left(\frac{hm}{\pi}\right)^{3/2} \int_0^{2\pi} d\phi \int_0^{\frac{\pi}{2}} dxdy \quad \sin\theta \cos\theta d\theta \int_0^{\infty} dr \int_0^{\infty} \Psi dc.$$

In this equation Ψ has the value given by

$$\Psi = c^4 \Xi e^{-\frac{\Xi r}{c}} e^{-hmc^2}\left[1 \pm \left\{\frac{1}{N}\frac{dN}{dz} + \left(\frac{3}{2h} - mc^2\right)\frac{dh}{dz}\right\}\right].$$

The two quantities N and h vary simultaneously, thus for simplification of the integrations it may be best to express one in terms of the other. This is accomplished by means of certain conditions defining the equilibrium in the gas. They are included in the three following statements:

1. The mass of gas passing across the xy plane in any given time in both directions along the z-axis must be equal. If it were not, the density of the gas would vary as a function of the time, which it obviously does not do by definition of pure conduction phenomenon.

2. There is no mass motion of the gas, hence the excess of momentum transfer parallel to the z-axis must be constant for every unit of cross-section of the xy plane.

3. Since the conditions for heat transfer assumed that the net quantity carried along the z-axis is the same throughout the area studied, the same criterion of equal net heat transfer for any unit area of cross-section of the xy plane must also hold.

These relations may be expressed in the form of equations, each of which contains an integral of the same form as the one considered above. The three integrals differ only in that in the first one, applying to condition 1, the factor $\frac{1}{2}mc^2$ is absent, that in the second, applying to condition 2, the $\frac{1}{2}mc^2$ is replaced by $mc \cos\theta$; while the third, applying to condition 3, is the original equation under consideration above.

In the integrals introduced by conditions 2 and 3 it may be assumed that N and h are linear functions of z. The first derivatives of these are then constant and where they are multiplied by r (in itself small) they may be neglected for the present treatment.

The first integral, depending on the transfer of heat by a net mass movement of the gas, may only be solved through a consideration of the relation between N, Ξ, and h. Such a relation is obtained through simple integrations in the form of

$$0 = \int_0^\infty \frac{c^4}{\Xi} e^{-hmc^2} \left\{ \frac{1}{N}\frac{dN}{dz} + \left(\frac{3}{2h} - mc^2\right)\frac{dh}{dz} \right\} dc.$$

Originally, O. E. Meyer integrated this equation making two approximate assumptions representing extreme conditions. Taking a mean value of these two results, he arrived at a relation between N and h from this process that says that $\frac{1}{N}\frac{dN}{dz} = \frac{3}{4}\frac{1}{h}\frac{dh}{dz}$. W. Conrau actually integrated the correct expression by mechanical quadratures and found, instead of $\frac{3}{4}$ as the numerical factor, a factor 0.71066. Thus $\frac{1}{N}\frac{dN}{dz} = 0.71066\,\frac{1}{h}\frac{dh}{dz}$.* Substituting this for $\frac{1}{N}\frac{dN}{dz}$ one at once has Ψ in a simplified form.

$$\Psi = c^4 \Xi e^{-\frac{\Xi r}{c}} e^{-hmc^2} \left\{ 1 - \left(\frac{2.21066}{h} - mc^2\right) \frac{dh}{dz} \cos\theta \right\}.$$

Integration of Q, as far as is directly possible, for values of z above the xy plane and below it lead, on addition, to the net heat transfer per unit time as

$$\frac{dQ}{dt} = -Kdxdy\frac{dT}{dz} = -\frac{2\pi}{3} Nm \frac{dh}{dz}\left(\frac{hm}{\pi}\right)^{3/2} \int_0^\infty \frac{c^4}{\Xi}\left(\frac{2.2107}{h} - mc^2\right) e^{-hmc^2} dc$$

* Equilibrium of mass distribution throughout the gas is one of the conditions of equilibrium on which the distribution law is founded. In assuming $N \, a \, f(z)$, an assumption was introduced contrary to this law. It lead to the relation above

$$\frac{1}{N}\frac{dN}{dz} = 0.71066\,\frac{1}{h}\frac{dh}{dz}.$$

Had equality of density obtained, this expression would have been

$$\frac{1}{N}\frac{dN}{dz} = \frac{1}{h}\frac{dh}{dz}.$$

This discrepancy Jeans points out is the order of magnitude of the error introduced by the assumption of the distribution law holding accurately.

It is then necessary to reduce hm and $m\frac{dh}{dz}$ to terms containing the temperature T and C_v the specific heat at constant volume. Conversion of the units to heat units and comparison with the experimental equation of heat conduction $-K\frac{dT}{dz}dxdy$ leads to the evaluation of K in the following form:

$$K = \frac{8}{9\sqrt{\pi}}NC_v h^{\frac{3}{2}} m^{\frac{3}{2}} \int_0^\infty \frac{c^6}{\Xi}\left(mc^2 - \frac{2.2107}{h}\right) e^{-hmc^2}dc.$$

Again, in earlier papers Meyer integrated this by a method of approximation. At a later date, however, P. Neugebauer carried out the accurate integration and found that the value of the integral was such that K is given by

$$K = 0.5205\ Nm\bar{c}LC_v.$$

Since

$$\eta = \frac{1}{3}Nm\bar{c}L,$$

$$K = 1.53\eta C_v.$$

If Meyer's value of η be used where $\eta_m = \frac{1}{\pi}m\bar{c}L$

$$K = 1.6027\ C_v\eta_m$$

where η_m is Meyer's value of η.

Thus it is seen that a rigorous deduction brings a numerical factor into the relation $\frac{K}{\eta C_v}$ which is greater than unity. This factor is generally designated as ϵ and one may most properly write that

$$K = \epsilon\eta C_v$$

where ϵ varies from 1 to 2.57, depending on the mathematical analysis. The value of ϵ from theory, then, is not definite and depends on the extent to which approximations were made in deduction and how it was deduced.

Jeans[6] carries out essentially the same analysis as Meyer but includes certain terms expressing the variation of collision frequency omitted by Meyer.

Jeans further departs from Meyer in that he considers more in detail the contribution of energy given by each molecule when it moves from T_1 to T_2. Up to the point where the energy transfer is considered, Jeans follows Meyer's method. He obtains the expression for the net flow of molecules with velocities between c and $c + dc$ in the z direction as

$$\delta n_c = \frac{4}{3\pi\sigma^2\sqrt{hm}\Psi(x)}(x^2 - 2.21066)\frac{1}{h}\frac{dh}{dz}x^5e^{-x^2}dx,$$

where $x^2 = hmc^2$, and $\dfrac{\sqrt{\pi}N\sigma^2}{hmc}\Psi(c\sqrt{hm}) = \Xi$, the mean collision frequency. Now each of these molecules carries $\frac{1}{2}mc^2$, or $\frac{x^2}{2h}$, of energy of translation across the xy plane. Thus the heat energy of translation transferred is $\frac{x^2}{2hJ}$ per molecule, where J is the mechanical equivalent of heat. If Γ_t denotes all the heat transferred in this fashion, then on integration

$$\Gamma_t = \sum_{x=o}^{x=\infty}\frac{x^2}{2hJ}\delta n_c = \frac{2}{3h^2J\pi\sigma^2\sqrt{hm}}I\frac{dh}{dz},$$

where

$$I = \int_0^\infty \frac{(x^2 - 2.21066)}{\Psi(x)}x^7e^{-x^2}dx.$$

Now, as will be shown in Chap. IX, each molecule, if polyatomic, carries the energy g of which part is translational part rotational, and part vibrational in the molecule. Jeans calls the ratio of internal (including vibrations along the line of juncture of the molecules as well as rotational (see Sec. 91, Chap. IX)) to the translational energy, β. Now it is not certain that the transfer of internal energy is equal to β times the translational, for, as Jeans points out, the internal energy coming from dv is not β times $\frac{mc^2}{2}$ where c is the velocity of the molecule, but is β times $\frac{1}{2}\overline{mc^2}$, where $\overline{mc^2}$ is the average value of mc^2 in dv. The internal energy to be expected is, then $\frac{3}{4}\frac{\beta}{h}$, where h is evaluated in the element dv, or $\frac{3}{4}\frac{\beta}{h} + \frac{3}{4}r\cos\theta\,\frac{\beta}{h^2}\frac{dh}{dz}$. This follows, since $\frac{1}{2}\overline{mc^2} = E = \frac{3}{2}kT$ and $kT = \frac{1}{2h}$, therefore $\frac{1}{2}\overline{mc^2} = \frac{3}{4h}$. This contribution to the energy flow must be included in the original differential equations. It leads to integrations which cannot be evaluated in finite terms, and the problem remains unsolved. Roughly, Jeans assumes that one may write $\Gamma_i = \beta\Gamma_t$, or, more strictly, $\Gamma_i = A\beta\Gamma_t$, where A is a number which cannot be calculated. Jeans qualitatively demonstrates that A must be less

than unity, as follows. It is obvious that it is the molecules with long free paths that are efficient as energy carriers. On the average, however, these long free-path molecules must have the greater energy of translation. Thus, while they have a greater translational energy, their internal energy does not correspond to this same high value, since the internal energy is not connected with efficient transfer. Hence A must be a factor which makes $A\beta\Gamma_t$ less than the maximum to be expected $\beta\Gamma_t$.

Since the total heat transfer is

$$-K\frac{dT}{dz} = \frac{K}{2h^2R}\frac{dh}{dz},$$

this must equal

$$\Gamma_t + \Gamma_i = (1 + A\beta)\Gamma_t,$$

whence

$$K = \frac{4(1 + A\beta)R}{3J\sigma^2\sqrt{hm}}I.$$

If $A = 1$, $c = \dfrac{2}{\sqrt{\pi hm}}$ and $C_v = \dfrac{3}{2}(1 + \beta)\dfrac{R}{Jm}$ (see Sec. 92),

$$K = \frac{4Im}{9\sqrt{\pi}\sigma^2}\bar{c}C_v.$$

For viscosity, if persistence of velocities be left out, Jeans found

$$\eta = \frac{1}{3}\rho\bar{c}L = \frac{1}{3}\rho\bar{c}\left[\frac{1.051}{\sqrt{2}\pi N\sigma^2}\right],$$

where 1.051 is the constant for the free path.

Thus
$$K = \frac{4}{3}\frac{I\sqrt{2\pi}}{1.051}\eta C_v.$$

King[9] has performed the integrations of the factor $I_n = \int_0^\infty \frac{x^n}{\Psi(x)}e^{-x^2}dx$ and finds I_9 to be 1.4625, and I_7 to be 0.4631. Thus $I = I_9 - 2.21066\, I_7 = 0.4387$.

Hence
$$K = 1.395\eta C_v.$$

This equation has not been corrected for persistence of velocities. Both η and K, however, are proportional to the mean free path and hence both are equally affected by the persistence of velocities, hence $\dfrac{K}{\eta}$ will be little affected by this correction and the equation stands. This value of ϵ may be improved according to Jeans[6] by the introduction of a factor $\dfrac{1}{(1 - \frac{1}{2}\theta)}$ inside the

integrand for the value of I above, where Θ depends on the persistence of velocities. Making this correction in analogy to a correction used in the case of viscosity, Jeans obtains

$$K = 1.497\eta C_v.$$

This value of ϵ is about that which Meyers obtained in setting $\eta = \frac{1}{3}Nm\bar{c}L$, which was 1.53.

Chapman,[7] proceeding on entirely different lines, found ϵ for all monatomic gases for laws of force between the molecules of the form μr^{-S}, including the case where $S = 5$ studied by Maxwell.[10] The value found to a first approximation, which is correct to within a few per cent as shown by further approximations, gives $\epsilon = 2.500$. Enskog[8] found a complicated expression for ϵ, which reduces to 2.5 when $S = 5$. These values are concordant and higher than the values deduced on the simple mechanical picture.

The values of ϵ observed for the monatomic gases by various observers are as follows (see Jeans[6]):

He	0°C.	2.40
	−191.6°C.	2.23
	−252.1°C.	2.02
Ar	0°C.	2.49
	182.5°C.	2.57
Neon	10°C.	2.501

Schwarze found for He, 2.507; for Ar, 2.501; Hercus and Soby for He, 2.31; for Ar, 2.47. Thus the law as deduced by Chapman and Enskog appears to be correct.

The values of $\dfrac{K}{\eta C_v} = \epsilon$ observed for a number of gases is given in the accompanying table.

	ϵ obs.	$\frac{1}{4}(9\gamma - 5)$
H_2	1.91	1.90
He	2.38	2.44
CO	1.88	1.91
N_2	1.91	1.91
C_2H_4	1.55	1.55
Air	1.91	1.91
NO_2	1.86	1.88
O_2	1.90	1.90
Ar	2.49	2.44
CO_2	1.55	1.72
N_2O	1.76	1.73

When β is 0, ϵ is largest, and when β is large, ϵ has its lowest values. This Jeans points out may come largely from the ignoring of the factor A by which β should have been multiplied.

If the simple equation which was deduced at the beginning of this discussion, had been taken, to wit,

$$K = \eta C_v,$$

another approximation can be made. This may be written

$$K = \eta C_v = \frac{3}{2}(1 + \beta)\frac{R}{mJ}\eta,$$

where C_v has been replaced by its equivalent in rotational and internal energy, β being the ratios of these energies to translational energy present.

Since experimentally for monatomic gases when $\beta = 1$

$$K = \frac{5}{2}C_v\eta = \frac{5}{2}\left(\frac{3}{2}\frac{R}{Jm}\right)\eta$$

and not

$$K = \frac{3}{2}\frac{R}{Jm}\eta = C_v\eta,$$

as simple theory would have it, it may be proper to increase arbitrarily the factor 1 in the general equation for C_v by the factor $5/2$. Thus the correct equation for K would be

$$K = \frac{3}{2}\left(\frac{5}{2} + \beta\right)\frac{R}{Jm}\eta$$

or

$$K = \frac{5/2 + \beta}{1 + \beta}\eta C_v$$
$$= \frac{1}{4}(9\gamma - 5)\eta C_v,$$

where γ is the ratio of the specific heats. This expression for K leads to values of $\epsilon = \dfrac{K}{\eta C_v}$ which agree fairly well with the observed values as seen in column 3 of the table above. It must be borne in mind, however, that this agreement is forced by the introduction of the arbitrary factor $5/2$ in the place of unity in the simple equation, as a result of the values found for monatomic gases, and the values from the treatments of Chapman and Enskog.

From these considerations it may be concluded that, in order of magnitude, the value for K can be correctly predicted by the

kinetic theory. There still remains a numerical factor ϵ whose value yielded by the theory up to the present is not quite satisfactory. The difficulty chiefly lies in the mathematical complexity introduced by all the conditions which determine its existence.

As regards the variation of K with pressure, and temperature, the same may be said as for viscosity, except that the variations of C_v with these factors must be taken into account. Thus K, the coefficient of heat conductivity, should be independent of pressure to the extent that C_v is independent of pressure. This was first enunciated by Maxwell.[11] It was confirmed experimentally first by Stefan[12] and later by others. This surprising law was found to hold from pressures at which convection ceased down to quite low pressures which are of the order of a mm of mercury. At still lower pressures K becomes less. But this action is due to the fact that below these pressures the mean free path becomes comparable to the dimensions of the vessel and the mechanism of heat transfer must be analyzed from a different standpoint (see Sec. 80). Again, assuming C_v constant, K should, as is the case for η, be theoretically proportional to the square root of the absolute temperature. It was found, however, that, owing to the decrease in the action of intermolecular forces with increasing temperature (*i.e.*, the apparent decrease of the diameter of the molecules from this cause) the mean free paths, and hence the coefficient of viscosity, increased more rapidly than with the square root of the absolute temperature. Thus K should vary in the same manner with temperature as η does, that is, K should increase with T faster than proportional to $\sqrt{T}$. Some preliminary experiments by Winkelmann[13] seemed to indicate this to be true. Measurements of K are, on the whole, very difficult and inaccurate in gases because of the difficulty in eliminating convection and radiation. Later experiments above 0°C. seemed to indicate that K increased less rapidly with T than the value of η. In fact, some experiments indicated that K was more nearly proportional to $\sqrt{T}$. *The results of the many experiments are none the less quite discordant, and little can be concluded from them.* Below 0°C. a much more rapid decrease in K with a decrease in T was noted, as was observed to be the case for viscosity and as is predicted by the theory of Sutherland[14] for viscosity. The conclusion to be drawn is that, in general, K shows the same trend with temperature that η exhibits, although the variation may not be accurately parallel.

On the whole, however, the success of the kinetic theory in predicting and evaluating the heat conduction has been striking, and the unexpected agreement of the predicted constancy of K with pressure variation was, indeed, a dramatic triumph. Needless to say, the inaccuracy of the measurements of K and the large uncertainty in ϵ make this coefficient of little use in determining L, the mean free path.

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III. DIFFUSION

70. Definition of Diffusion.—If a gas of one sort be confined in a vessel adjoining another vessel filled with a different gas at the same pressure, and if the vessels be suddenly made to communicate with each other, the first gas will slowly spread throughout the two vessels until its concentration is uniform. The other gas will simultaneously move in such a manner as to distribute itself equally throughout the space in both vessels. This phenomenon is known as the interdiffusion of the two gases. If the attention be fixed on one gas only, the statement may be made that it diffuses into the other gas and the time rate of this process

may be studied. Fixing one's attention on the one gas, it has *been assumed from experiment* that, for the steady state, the number of molecules N diffusing through a given area $dxdy$ in a time dt may be expressed by the relation

$$N_{dxdydt} = -D \frac{dN}{dz} dtdxdy.$$

In this equation $\frac{dN}{dz}$ is the rate of change in the number of molecules of the gas per unit volume (*i.e.*, the concentration) along the z-axis normal to the xy plane. D is a constant of proportionality and depends on the gases in question. The concentration gradient $\frac{dN}{dz}$ is the cause of the process of diffusion and is proportional to the partial pressure gradient $\frac{dp}{dz}$ of the gas. The sign is negative since the transfer takes place from higher values of N to lower ones.

Obviously, the constant D depends on the rate at which the molecules can move across the area $dxdy$ as a result of the gradient of their partial pressure p. This, as with all pressure phenomena, is, obviously, caused by the heat motions, and the problem then merely devolves itself into one of determining the net number of molecules moving across a given area under a concentration gradient due to their proper heat motions. The phenomenon of diffusion also occurs in liquids and solids, and in both of these the general laws are the same. As is the case in viscosity and heat conduction, the effect of the intense intermolecular forces in these latter two cases, however, complicates the problem, and the treatment that is given for the case of gases does not apply.

While fixing the attention on the molecules of one kind simplifies the analysis from the mathematical point of view, it greatly restricts the applicability of the results to the more general cases, for unless the diffusion occur for one kind of molecules into a gas composed of molecules of the same mass velocity, and free paths, the equation is incomplete. In general, then, the interdiffusion of molecules must really be treated. To this end a gas may be considered in which the pressure is everywhere the same and which consists of two kinds of molecules, A and B, the composition varying from layer to layer along the vertical z-axis, being constant, however, parallel to the x- and y-axes. Call m_A

and m_B the masses and N_A and N_B the number of the two kinds of molecules per cm³. It is convenient to express the composition by the variable mol fraction F of A, where this may be defined as

$$F = \frac{N_A}{N_A + N_B}.$$

Then by experiment it is found that the mass of A diffusing downward across the element of area $dxdy$ of the plane $z = z_0$ in a time dt may be assumed to be given by the expression

$$d(m_A N_A)_{z0} = -D\frac{dF}{dz} m_A N dxdydt.$$

In this treatment $N\frac{dF}{dz}$ is the same as the concentration gradient $\frac{dN}{dz}$ used in the simpler case.

If, now, one considers a cylinder of base $dxdy$ and height Δz parallel to the z-axis the mass diffusing into the cylinder in dt is given by the expression above. The mass diffusing out of the cylinder at the point $z = z_0 + \Delta z$ is then given by

$$d(m_A N_A)_{z+\Delta z} = m_A N dxdydt\left[D\frac{\partial F}{\partial z} + \frac{\partial}{\partial z}\left(D\frac{\partial F}{\partial z}\right)\right]\Delta z.$$

The difference of the quantities entering and leaving the cylinder gives the accumulation of molecules A in the cylinder in the time dt as

$$m_A N dxdy\Delta z dt\frac{\partial}{\partial z}\left(D\frac{\partial F}{\partial z}\right).$$

This quantity is also the time rate of increase of the mass of A molecules in the cylinder, that is,

$$m_A N.\frac{dF}{dt} dxdy\Delta z dt.$$

Putting these two quantities equal to each other,

$$m_A N dxdy\Delta\, zdt\frac{\partial}{\partial z}\left(D\frac{dF}{dz}\right) = m_A N\frac{\partial F}{\partial t} dxdy\Delta z dt$$

or

$$\frac{\partial F}{\partial t} = \frac{\partial}{\partial z}\left(D\frac{\partial F}{\partial z}\right).$$

If D be assumed independent of z, one may write $\frac{\partial F}{\partial t} = D\frac{\partial}{\partial z}\left(\frac{\partial F}{\partial z}\right).$

This latter equation says that the rate of increase of the mol fraction of molecules with the time is the diffusion coefficient

multiplied into the rate of change of the mol fraction concentration gradient $\frac{\partial F}{\partial z}$ with z.

This expression is exactly the same as the Fourrier[1] equation for heat conduction in a solid body. In the latter case the quantity F would be replaced by T, the temperature, and D would be replaced by h^2, the "temperature diffusivity" of the substance, where $h^2 = \frac{K}{\rho c}$, K being the coefficient of heat conductivity, c the specific heat, and ρ the density of the substance. Both these equations in practical application assume h and D independent of T or F. This, although not strictly true, is sufficiently correct for the solution of most problems.* Thus all the classical solutions of the Fourrier heat equation may be carried over to the case of diffusion with the modifications indicated. In the present discussion, as is done practically with heat, it is often simpler to deal with cases in which a steady state has been approximated, that is, the experiments are performed in such a manner as to make $\frac{dF}{dt} = 0$. Then $\frac{dF}{dz}$ takes on a constant value, and experimental measurement and discussion are simplified. This is the case in the simple treatment given in Sec. 71.

Some notion of the phenomenon, may be gained from the table below, which gives the values of D for some of the commoner substances. The diffusion coefficients are given as the mass of the diffusing gas which crosses 1 cm^2 per second when there is unit concentration gradient present at the point (*i.e.*, when $\frac{d(m_A N_A)}{dz} = 1$ gram per cm^3 per cm along z). In fact, it makes no difference in what units the diffusion is expressed as long as

* The variation of D with F, when it occurs, gives rise to an apparent mass motion of the gas. This may be seen by carrying out the differentiation, assuming D to be a function of F and hence of z.

$$\frac{\partial F}{\partial t} = D\frac{\partial^2 F}{\partial z^2} + \frac{\partial D}{\partial z}\frac{\partial F}{\partial z}.$$

The increase of $\frac{\partial F}{\partial t}$ due to the variation of D with F is that which would result if the gas were to have a mass motion with a velocity $w_0 = -\frac{dD}{dz}$ for the quantity $\frac{dD}{dz}$ has the dimensions $\frac{L}{T}$. That this is so will be seen in Sec. 72.

the gradient and the number are expressed in terms of the same units, for $D = \dfrac{N_{dxdydt}}{\dfrac{dN}{dz}\,dxdydt}$.

Gas diffusing	Gas diffused into	D	t, in degrees centigrade
H_2	O_2	0.677	0
H_2	CO_2	0.538	0
O_2	N_2	0.171	0
O_2	H_2	0.722	0
CO_2	N_2O	0.15	0
C_2H_5OH	Air	0.102	0
C_2H_5OH	CO_2	0.068	0
C_2H_5OH	H_2	0.378	0

Substance diffusing	Solute	D for 1 sec.
Glycerine	Water	7.83×10^{-6}
Acetamide	Water	10.4×10^{-6}
Mannose	Water	5.62×10^{-6}
HCl	Water	2.66×10^{-5}
NaCl	Water	1.28×10^{-5}
$NaCH_3CO_2$	Water	9.02×10^{-6}

In solids the rate is far slower yet, and it is interesting to note the large difference in the values of D for gases and for solutions.

71. The Theory of Self-diffusion of Molecules.—Consider molecules of a certain mass and diameter diffusing into a gas of molecules of similar mass and diameter. The phenomenon is known as self-diffusion. Assume that a uniform rate of flow has been established, that is to say, that $\dfrac{dN}{dt} = 0$. Under these conditions the molecules have reached an equilibrium state and a linear concentration gradient $\dfrac{dN}{dz}$ along the z-axis has been obtained. Assume, further, that the concentration decreases from above downwards. The state pictured would be nearly achieved if molecules from an indefinitely large vessel of CO_2 were diffusing along a long tube into an indefinitely large chamber of N_2O molecules. After some time the rate of change

in concentration at one point in the tube would have ceased and the concentration at any point z above an arbitrarily chosen xy plane normal to the tube would be given by $N + z\frac{dN}{dz}$, where N is the number of molecules per cm^3 at $z = 0$, or at the xy plane. Below the plane at a point z the number of molecules would be $N - z\frac{dN}{dz}$. Consider now an area $dxdy$ in the xy plane. At L cm above it there will be $N + L\frac{dN}{dz}$ molecules. If L is the average free path, $1/6$ of the molecules moving with a velocity $\bar{c}$ will have velocities directed so as to pass down through $dxdy$ on their next free path. The number of molecules in a layer dL in height and of base $dxdy$ is $dxdydL\left(N + L\frac{dN}{dz}\right)$. These are the molecules which will in the next path pass through $dxdy$ downwards. Now the length dL may be represented by the molecules traveling with a velocity $\bar{c}$, which in a time dt pass through L. Hence the number of molecules passing from the volume $dxdydL$ or $dxdy\bar{c}dt$ through the area $dxdy$ as a result of the concentration gradient in the time dt will be the number that lie in this cylinder multiplied by the fraction which have velocities $\bar{c}$ in the direction z such that they will pass through $dxdy$, that is,

$$N_{dt\downarrow} = -\frac{1}{6}\,dxdy\bar{c}dt\left(N + L\frac{dN}{dz}\right),$$

the $-$ sign denoting that the molecules are passing from higher values of N to lower values. In a similar manner, the number of molecules passing from the layer L below xy upwards through $dxdy$ in dt will be

$$N_{dt\uparrow} = +\frac{1}{6}\,dxdy\bar{c}dt\left(N - L\frac{dN}{dz}\right).$$

The total net transfer of molecules through $dxdy$ will be

$$N_{dt} = N_{dt\downarrow} + N_{dt\uparrow}$$

or

$$N_{dt} = -\frac{1}{3}\,dxdy\bar{c}dtL\frac{dN}{dz}.$$

The number passing per unit time will then be $N_{dxdy} = \frac{N_{dt}}{dt}$, whence the number of molecules diffusing through $dxdy$ per second will be

$$N_{dxdy} = -\frac{1}{3}\,dxdy\frac{dN}{dz}\bar{c}L.$$

But this has been shown by experiment to be given by

$$N_{dxdy} = -D\frac{dN}{dz}dxdy.$$

Whence

$$D = \frac{1}{3}\bar{c}L.$$

This is the coefficient of diffusion as defined for the simple case.

Since $\eta = \frac{1}{3}Nm\bar{c}L$ it follows at once that $D = \frac{\eta}{Nm}$. But mN is ρ, the density, so that one may write $D = \frac{\eta}{\rho}$.

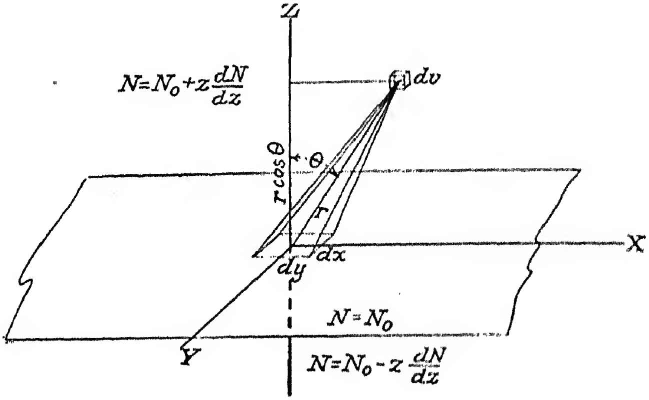

FIG. 41.

The same expression may be derived in a more rigorous fashion, taking into account the distribution of free paths and velocities. Assume, as before, that the steady state has been reached and that the concentration above and below the xy plane may be represented by $N + z\frac{dN}{dz}$, and $N - z\frac{dN}{dz}$. Consider an element of volume dv above the xy plane at a distance r from the area $dxdy$, such that the line from dv to $dxdy$ makes an angle θ with the normal to $dxdy$, Fig. 41. Thus $z = r\cos\theta$. Each of the molecules in dv has a mean free path L and a velocity c, then each molecule *starts a new free path* $\frac{c}{L}$ times a second. Now in dv there are $dv\,\frac{4}{\alpha^3\sqrt{\pi}}c^2e^{-\frac{c^2}{\alpha^2}}dc\left(N + r\cos\theta\,\frac{dN}{dz}\right)$ molecules with a velocity between c and $c + dc$. Of these, the number in a cone

of base $dxdy \cos\theta$ and height r will have velocities directed towards $dxdy$, that is,

$$\frac{dxdy\cos\theta}{4\pi r^2}\frac{4}{\alpha^3\sqrt{\pi}}\frac{c^3}{L}e^{-\frac{c^2}{\alpha^2}}dcdv\left(N + r\cos\theta\frac{dN}{dz}\right).$$

will start for $dxdy$ per second. But, of these, only the fraction $e^{-\frac{r}{L}}$ will have paths exceeding r and will, accordingly, be able to pass through $dxdy$ without impact. Hence the number of molecules from dv passing downward through $dxdy$ per second will be

$$N_{dv\downarrow} = \frac{dxdy\cos\theta dv}{4\pi r^2}e^{-\frac{r}{L}}\frac{4}{\alpha^3\sqrt{\pi}}\frac{c^3}{L}e^{-\frac{c^2}{\alpha^2}}dc\left(N + r\cos\theta\frac{dN}{dz}\right).$$

Expressing dv in terms of the polar coordinates, $dv = (dr)(rd\theta)$ $(r\sin\theta\, d\phi)$, one has the number $N_{dv\downarrow}$ given as

$$N_{dv\downarrow} = \frac{dxdy}{\pi L}\frac{c^3}{\alpha^3\sqrt{\pi}}e^{-\frac{c^2}{\alpha^2}}dce^{-\frac{r}{L}}\cos\theta\sin\theta d\theta d\phi\left(N + r\cos\theta\frac{dN}{dz}\right).$$

In a similar fashion the number passing from a volume dv below the xy plane may be found to be

$$N_{dv\uparrow} = \frac{dxdy}{\pi L}\frac{c^3}{\alpha^3\sqrt{\pi}}e^{-\frac{c^2}{\alpha^2}}dce^{-\frac{r}{L}}\cos\theta\sin\theta d\theta d\phi\left(N - r\cos\theta\frac{dN}{dz}\right).$$

These expressions must now each be integrated for c from 0 to ∞, for r from 0 to ∞, for θ from 0 to $\frac{\pi}{2}$, and for ϕ from 0 to 2π to give the total numbers of molecules of all velocities passing through $dxdy$ from the volumes above and below the xy plane. Integration gives

$$N_\downarrow = \left\{\frac{N\bar{c}}{4} + \frac{dN}{dz}\frac{\bar{c}}{6}L\right\}dxdy.$$

$$N_\uparrow = \left\{\frac{N\bar{c}}{4} - \frac{dN}{dz}\frac{\bar{c}}{6}L\right\}dxdy.$$

To get the total number passing through $dxdy$ these expressions would have to be added, remembering that $N_\downarrow$ has the negative sign, for the molecules are moving from a region of higher concentration to one of lower concentration. Hence $N_{dxdy} = -N_\downarrow + N_\uparrow$

or
$$N_{dxdy} = -\frac{1}{3}\bar{c}L\frac{dN}{dz}dxdy.$$

Since by experiment for the steady state

$$N_{dxdy} = -D\frac{dN}{dz}dxdy,$$

then at once $D = \frac{1}{3}\bar{c}L$, which was the result arrived at before in a much more elementary fashion. It might be added in passing that had $\frac{dN}{dz}$ been 0, N_{dxdy} would have been 0. For this case $N\downarrow$ equals $N\uparrow = \frac{N\bar{c}}{4}$, that is, one would have found the number of molecules striking a square cm per second from above or below to be $\frac{N\bar{c}}{4}$. This result was obtained in Sec. 40.

72. The Theory of Interdiffusion.—In this section the more general treatment of the interdiffusion to two gases A and B will be taken up where the masses of the molecules A and B are not equal. In what follows use will be made of the mol fraction, and the notation in the latter part of Sec. 70 will apply.

As the temperature is constant throughout the gases the *most probable speeds* of the A and B molecules α_A and α_B will be different as a result of the equipartition of energy. Thus

$$m_A\alpha_A^2 = m_B\alpha_B^2.$$

It will be assumed that the variations of F, the mol fraction of A, with z are so small over a free path that the distribution of velocities of the two kinds of molecules may be considered Maxwellian.

Although the molecular density remains constant in pure diffusion, since the total pressure is everywhere the same, the changing composition means a change in the mass density. This means that there is a mean mass velocity of the gas in the direction of diffusion. Let this velocity, which is very small, be denoted by w_o. It is a mass velocity of the molecules along the z-axis of coordinates, diffusion taking place along the z-axis as assumed in Sec. 71. Owing to the presence of this mass motion velocity, w_o, the number of molecules having components along the various axes, is no longer the same. Out of N molecules of the type A, $\frac{N}{\alpha_A\sqrt{\pi}}e^{-\frac{u^2}{\alpha_A^2}}du$ will have velocities between u and $u + du$, and $\frac{N}{\alpha_A\sqrt{\pi}}e^{-\frac{v^2}{\alpha_A^2}}dv$ molecules will have velocities

between v and $v + dv$, but $\frac{N}{\alpha_A\sqrt{\pi}}e^{-\frac{(w-w_o)^2}{\alpha_A^2}}dw$ molecules will have velocities between w and $w + dw$ owing to the component w_o, for the velocity w is composed of the mass velocity w_o and the translational heat velocity $w - w_o$. Maxwell's law applies to the translational velocities only, and these must be included. This will be $w - w_o$ for the positive component, and $-w + w_o$ for the negative component. Both terms represent the difference in two velocities. The sign of the whole expression is immaterial, since the term is squared. The number of molecules having velocity components between u and $u + du$, v and $v + dv$, and w and $w + dw$ simultaneously is, then,

$$\frac{N}{\alpha_A{}^3\pi^{3/2}}e^{-\frac{[u^2+v^2+(w-w_o)^2]}{\alpha_A{}^2}}dudvdw.$$

At a point in the gas where the mol fraction has a value F there will be F times the number of A molecules with velocities lying within the limits specified above. Of these, those lying in a volume, $w\ dtdxdy$ will pass through an area $dxdy$ in a time dt. The total number which will pass through this area in dt requires integration from $-\infty$ to $+\infty$ for the u and v components, and from 0 to ∞ for the w component if only the transfer from above downward is regarded. For the net transfer the integration would have to be carried from $-\infty$ to $+\infty$ for the w component as well. Thus the net number of A molecules crossing $dxdy$ in the plane $z = z_o$ in the time dt is given by

$$\frac{Ndtdxdy}{\alpha_A{}^3\pi^{3/2}}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} Fwe^{-\frac{u^2+v^2+(w-w_o)^2}{\alpha_A{}^2}}dudvdw.$$

This expression will not vanish for two reasons: First, because of the component of streaming motion w_0, and, second, because F has different values on the two sides of the xy plane. Now the molecules which pass through the area $dxdy$ are only those that had their last collision a free path away, that is, only those molecules which started anew from a collision L cm away will pass through $dxdy$. Thus the value of F chosen is the one which corresponds to the scene of the last impact. If the molecular path makes an angle θ with the z-axis, this distance will be $L \cos\theta$ distant from z_o. For a steady state or where F does not change rapidly with the distance, one may write

$$F = F_o + \left(\frac{dF}{dz}\right)_0 L\cos\theta.$$

Moreover, since w_o is small compared to α_A, one may write $e^{-\frac{(w-w_o)^2}{\alpha_A{}^2}} = \left(1 + \frac{2ww_o}{\alpha_A{}^2}\right) e^{-\frac{w^2}{\alpha_A{}^2}}$. With these substitutions, the expression for the net number of A molecules crossing *unit area* in a time dt becomes:

$$\frac{Ndt}{\alpha_A{}^3\pi^{3/2}}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\left[F_o + L\ \cos\ \theta\left(\frac{\partial F}{\partial z}\right)_0\right]w\left(1 + \frac{2ww_o}{\alpha_A{}^2}\right) e^{-\frac{u^2+v^2+w^2}{\alpha_A{}^2}}\,dudvdw.$$

This may be transformed to an expression in the polar coordinates c, θ, and ϕ, as in Sec. 35, and then becomes

$$\frac{Ndt}{\alpha_A{}^3\pi^{3/2}}\int_0^{\infty}dc\int_0^{2\pi}d\phi\int_0^{\pi}\left[F_o + L\ \cos\ \theta\left(\frac{\partial F}{\partial z}\right)_0\right]\left(1 + 2\frac{w_oc}{\alpha_A{}^2}\cos\ \theta\right) c^3e^{-\frac{c^2}{\alpha_A{}^2}}\sin\ \theta\ \cos\ \theta d\theta.$$

Integration with respect to ϕ gives the factor 2π. Multiplication and neglect of small terms of higher order than the first one gives

$$\frac{2Ndt}{\alpha_A{}^3\sqrt{\pi}}\int_0^{\infty}dc\int_0^{\pi}\left[F_o + 2F_o\frac{w_oc}{\alpha_A{}^2}\cos\theta + L\cos\theta\left(\frac{\partial F}{\partial z}\right)_0\right]c^3e^{-\frac{c^2}{\alpha_A{}^2}}\sin\theta\cos\theta d\theta.$$

Integration with respect to θ yields

$$\frac{4Ndt}{3\alpha_A{}^3\sqrt{\pi}}\int_0^{\infty}\left[2F_o\frac{w_oc}{\alpha_A{}^2} + L\left(\frac{\partial F}{\partial z}\right)_0\right]c^3e^{-\frac{c^2}{\alpha_A{}^2}}dc.$$

Assuming L independent of c, integration leads to the result

$$Ndt\left\{F_ow_o + \frac{1}{3}\left(\frac{\partial F}{\partial z}\right)\bar{c}_AL_A\right\}.$$

This is the net number of A molecules crossing the plane $z = z_o$ in the direction of the gradient. In a similar manner the expression for the B molecules diffusing from below the $z = z_o$ plane upwards may be found to be

$$Ndt\left\{(1 - F_o)w_o - \frac{1}{3}\left(\frac{\partial F}{\partial z}\right)_0\bar{c}_BL_B\right\}.$$

Here the concentration of B molecules is given by $(1 - F_o)$, where F_o is the mol fraction of A molecules, and the $-$ sign comes from the fact that the concentration of B molecules decreases as z increases.

Since the molecular density must remain constant everywhere, the total number of molecules crossing the plane must be 0, that is,

$$-Ndt\left\{(1 - F_o)w_o - \frac{1}{3}\left(\frac{\partial F}{\partial z}\right)_0 \bar{c}_B L_B\right\}$$

must equal

$$Ndt\left\{F_o w_o + \frac{1}{3}\left(\frac{\partial F}{\partial z}\right)_0 \bar{c}_A L_A\right\},$$

whence

$$-w_o = \frac{1}{3}\left(\frac{\partial F}{\partial z}\right)_0 \left\{\bar{c}_A L_A - \bar{c}_B L_B\right\}.$$

This value of w_o may be substituted into the expression for the number of A molecules diffusing through unit area in the $z = z_o$ plane in the time dt, which is

$$Ndt\left\{F_o w_o + \frac{1}{3}\left(\frac{\partial F}{\partial z}\right)_0 \bar{c}_A L_A\right\}$$

and gives the number at once in terms of the mol fractions of A molecules, the concentration gradient, and the free paths and average velocities of A and B molecules, to wit

$$Ndt\left[-F_o\frac{1}{3}\left(\frac{\partial F}{\partial z}\right)_0 \left\{\bar{c}_A L_A - \bar{c}_B L_B\right\} + \frac{1}{3}\left(\frac{\partial F}{\partial z}\right)_0 \bar{c}_A L_A\right]$$
$$= \frac{1}{3}Ndt\left(\frac{\partial F}{\partial z}\right)_0\left[(1 - F_o)\bar{c}_A L_A + F_o \bar{c}_B L_B\right].$$

The mass of A molecules crossing an area $dxdy$ in unit time is then merely this quantity multiplied by m_A and $dxdy$, whence

$$d(m_A N_A)_{dxdydt} = -\frac{1}{3}Ndt\left(\frac{\partial F}{\partial z}\right)_0 dxdy\left[(1 - F_o)\bar{c}_A L_A + F_o \bar{c}_B L_B\right] m_A.$$

But by definition

$$d(m_A N_A)_{dxdydt} = -DNdt\left(\frac{\partial F}{\partial z}\right)_0 dxdym_A.$$

Therefore

$$D = \frac{1}{3}\left[(1 - F_o)\bar{c}_A L_A + F_o \bar{c}_B L_B\right].$$

This is the classical expression for the interdiffusion of two gases in terms of their average speed and mean free paths.

It is of interest to notice in passing that the mass motion of the gas was given by

$$w_0 = -\frac{1}{3}\left(\frac{\partial F}{\partial z}\right)_0 \left\{\bar{c}_A L_A - \bar{c}_B L_B\right\}.$$

If the expression for D just found is differentiated with respect to F,

$$\frac{dD}{dF} = -\frac{1}{3}\left[\bar{c}_A L_A - \bar{c}_B L_B\right]$$

or

$$w_o = \left(\frac{\partial F}{\partial z}\right)_o \frac{\partial D}{\partial F},$$

which agrees with the formula found on purely hydrodynamic grounds in Sec. 70.

Since the viscosity of a gas is given by $\eta = \frac{1}{3}\rho\bar{c}L$ the expression for interdiffusion of the gases may be written as

$$D = F_o\frac{\eta_B}{\rho_B} + (1 - F_o)\frac{\eta_A}{\rho_A}.$$

73. Criticism of Transfer Theory.—This section contains a discussion of the theoretical results obtained in preceding sections, together with a statement of some results of theoretical investigations on diffusion the details of which are too advanced for inclusion in this book.

For simplicity, in the preceding discussion L was treated as a constant and placed in front of the integral sign. A more exact treatment would require that the expression for L_c, the mean free path of a molecule of speed c (Sec. 39) be used, and that the integration using this value be carried out. In Sec. 39 the value of L_c was found for a molecule of speed c moving in a pure gas. To be applicable above, it would be necessary to generalize the expression to the case of a gas consisting of two kinds of molecules. The results of such a generalization lead to a complicated definite integral which must be evaluated for each value of the mol fraction F. Tait[2] has carried the analysis to the point of setting up the very complicated integrals involved, but they have seemingly never been computed, so that one cannot say how this refinement would affect the theory.

The correction becomes considerably simpler when the gases A and B have the same molecular weight and the same diameter. In this case the most probable speeds α_A and α_B are equal, as are also the collision frequencies Z. Then L_c is given by the expression of Sec. 39. Using this in the theory, it is seen that the resulting integral is the same as that occurring in the viscosity

theory (Sec. 59), so that the result there given is applicable here. One has, then,

$$D = \frac{1}{3} \cdot \bar{c}L \cdot 1.051$$

as the coefficient of diffusion for two gases of equal molecular weight and diameter. The L here used is the Maxwell free path. The application of this correction does not change the relation $D = \frac{\eta}{\rho}$, since it affects both the diffusivity and the viscosity by the same amount.

Maxwell,[3] Boltzmann,[4] Chapman,[5] and Enskog[6] have contributed to the theory of diffusion by the study of the way in which Maxwell's law of distribution of velocities is affected by the variation in composition. These highly mathematical investigations fall outside the scope of this book. Some account of them is given in Jeans,[7] "Dynamical Theory of Gases," but for full treatment the student must consult the original memoirs.

It may be stated, however, that the effect of making these refinements in the theory is to introduce a factor ϵ somewhat greater than unity in the equation

$$D = \frac{\eta}{\rho}, \text{ that is, } D = \epsilon\frac{\eta}{\rho}.$$

For elastic spheres, Chapman finds that $\epsilon = 1.200$, *i.e.*, the self-diffusivity is 20 per cent greater than the simple theory indicates. For molecules repelling each other with a force inversely as the *fifth power* of the distance, Maxwell gave the exact theory and found that ϵ should equal 1.504. In Sec. 75, where a discussion of the results of experiments on diffusion is given, it will be seen that the experimental value of the ratio is contained within these limits.

74. Measurement of Gaseous Diffusion.—The first measurements of gas diffusion which were conducted in such a way that D could be evaluated from the data were made by Loschmidt[8] in 1870. The method he used is virtually the same as that used in all subsequent measurements of gas diffusion. He used a glass tube 97.5 cm long and 2.6 cm in diameter which was held in a vertical position. At its center it was divided into two parts by a partition. Initially, the top half was filled with the lighter of the two gases to be studied and the bottom half with the heavier. Then the partition between them was carefully removed and the

diffusion began. At a measured time later the partition was put back in place again. The contents of the two halves of the tube were then analyzed, and from the change in composition the value of the coefficient of diffusion was inferred.

It is desirable to give an account of the method in some detail in order to see what the experiments teach. The theory will be developed on the assumption that D does not depend on the composition of the gas at the place where the diffusion is taking place. Moreover, it will be remembered that when the diffusion equation was developed it was *assumed* that the mass of gas crossing unit area in unit time was simply proportional to the rate of change of the composition of the gas across that plane. Let it be supposed that a series of experiments like those just outlined were carried out, starting with the same gases but allowing different times to elapse before the partition was closed. If, now, the values of D inferred from each experiment in such a set should prove to be equal, the experiments would have confirmed the hypotheses made in the theory. If D should vary, however, it might be due to the fact that D is a function of the composition or to a more fundamental error coming from the assumption that the transfer of mass across a plane is not simply proportional to the composition gradient. The complete critical discussion of the experiments and their significance for these alternatives cannot be given in detail. The results will be given in the next section, where the measurements of D are summarized.

The theory of the Loschmidt method for the measurement of diffusion calls for the solution of the complete diffusion equation with appropriate boundary conditions. Let the length of the tube be a. Take the origin of x at the bottom so that the tube runs from $x = 0$ to $x = a$. At the initial instant, $t = 0$, assume the mol fraction F of A to be 1 from $x = 0$ to $x = \frac{a}{2}$ (*i.e.*, let it be assumed that there be only A molecules in the lower half and that above this point, from $x = \frac{a}{2}$ to $x = a$, there be none), also let it be assumed that there be only molecules of the B type in the upper half of the tube. Since no diffusion takes place through the ends of the tube, it follows also that

$$\frac{\partial F}{\partial x} = 0 \text{ at } x = 0 \text{ and } x = a \textit{ at all times.}$$

The solution of this problem for the conduction equation of Sec. 70 when $\frac{dF}{Dt} \neq 0$ is well known from the classical work in heat and is given in detail in works on partial differential equations, such as Byerly's[9] "Fourier Series and Spherical Harmonies." The solution is given in the form of a Fourier series and is as follows:

$$F = \frac{1}{2} + \frac{2}{\pi}\sum_{n=1}^{n=\infty} \frac{1}{n} \sin \frac{n\pi}{2} e^{-Dt\left(\frac{n\pi}{a}\right)^2} \cos \frac{n\pi x}{a}.$$

This infinite series expresses the mode of variation of F with the time at each place in the tube. In the experiments, the partition is replaced at the time t and the composition of the gas in the upper and lower halves of the tube determined by analysis. What is measured is the average value of F in each half of the tube. The measurements give F_L and F_u, the average values of F, in the lower and upper parts respectively. The averages can be computed in terms of D and t from the series by the formulæ:

$$\overline{F}_L = \frac{2}{a}\int_0^{\frac{a}{2}} F dx \quad \overline{F}_u = \frac{2}{a}\int_{\frac{a}{2}}^{a} F dx.$$

This yields for the two averages

$$\overline{F}_L = \frac{1}{2} + \frac{4}{\pi^2}\sum \frac{1}{n^2} \sin^2 \frac{n\pi}{2} e^{-Dt\left(\frac{n\pi}{a}\right)^2}$$

$$\overline{F}_u = \frac{1}{2} - \frac{4}{\pi^2}\sum \frac{1}{n^2} \sin^2 \frac{n\pi}{2} e^{-Dt\left(\frac{n\pi}{a}\right)^2}.$$

The difference in the mol fractions is, then,

$$\overline{F}_L - \overline{F}_u = \frac{8}{\pi^2}\left[e^{-\frac{\pi^2}{a^2}Dt} + \frac{1}{9}e^{-\frac{9\pi^2 Dt}{a^2}} + \frac{1}{25}e^{-\frac{25\pi^2 Dt}{a^2}} + \cdot \cdot \cdot\right].$$

In this expression the terms after the first three are so small for moderate values of t that they are quite negligible. It will be observed that the analysis of the contents of but one of the tubes is necessary, since if one is known the other follows from it directly. The manner in which D is to be computed from the above equation when $\overline{F}_L$, $\overline{F}_u$, a and t are known is rather involved and can only be carried out by successive approximations or graphical methods. In experimental work the times are such that the first three terms of the series only are necessary.

V. Obermayer[10] has given a table of values of $\bar{F}_L - \bar{F}_u$ computed from the series which greatly facilitates the evaluation of D from given data.

The following table is abridged from that of V. Obermayer. It refers to a tube for which $a = 86.62$ cm.

Difference in Mol Fraction as Function of Dt

Dt	$\bar{F}_L - \bar{F}_u$	Dt	$\bar{F}_L - \bar{F}_u$
0.00	1	0.06	0.368
0.01	0.738	0.07	0.323
0.02	0.632	0.08	0.283
0.03	0.549	0.09	0.248
0.04	0.480	0.10	0.218
0.05	0.420		

Stefan[11] employed another method of measuring diffusion. In it the gas is simply placed in a vertical cylindrical vessel. At the initial instant one end of the vessel (the upper one if the gas is heavier than air) is opened. After a measured time the cylinder is closed and the contents analyzed. The theory of this method proceeds along similar lines to that of the Loschmidt method. The diffusion equation must be solved with appropriate boundary conditions. If a is the length of the tube, the conditions assumed by Stefan are, at $t = 0$, $F = 1$ for $0 < x < a$; at all times, $\frac{\partial F}{\partial x} = 0$ for $x = 0$ and $F = 0$ at $x = a$. This last condition corresponds to the assumption that the gas escaping from the cylinder at the mouth diffuses outward in the three directions away from the mouth, so rapidly that the concentration is always zero at the mouth. This is, of course, not exactly correct, but requires a small end correction, *i.e.*, the actual accumulation of gas around the end makes the tube act as if it were slightly longer than it actually is. The theory of this correction does not seem to have been developed. It seems that the Loschmidt method is capable of greater accuracy than that of Stefan.

As was mentioned earlier in this section, if the assumptions leading to the differential equation of the diffusion are correct, the values of D obtained in a series of experiments should not depend on the period of time over which diffusion takes place.

Obermayer finds, however, small deviations of this sort such that, using the Loschmidt method, short periods of time invariably yield smaller values of the diffusivity than do longer periods of time. This led him to the conclusion that the mass transfer is not strictly proportional to the composition gradient, but is slightly less than proportionality would require for the large values of the composition gradient which occur during the first part of the experiments. All of these deviations are less than 4 per cent of the mean value of D. They do not seem to have been given theoretical discussion.

In the measurements made by students at Halle to determine the amount of dependence of D on the composition of the gas mixture, the Loschmidt method was employed in a slightly modified form. It is interesting to note that, as but slight dependence on the composition ratio was expected, these workers used the solution of the differential equations which assume D constant. This was necessary since the equations with D variable do not yield to solution. The work was so arranged that the composition did not vary much in an experiment, so the assumed constancy of D in the treatment is probably fairly correct. In some measurements, instead of putting pure A in one-half of the tube and pure B in the other, pure A was allowed to diffuse against a mixture of A and B of known initial composition. From such data, values of D were obtained as a function of the mean composition of the diffusing mixture. In other experiments the upper half of the tube was further subdivided into two equal parts and computations of the diffusivity based on analysis of all three compartments.

75. Experimental Results on Diffusion.—The measurement of diffusivity of gases can afford several crucial tests of the kinetic theory of gases and also yields valuable data on the size of molecules. The main result of the theory is that the diffusivity of a mixture of two gases is given by:

$$D = \epsilon\left[F\frac{\eta_B}{\rho_B} + (1 - F)\frac{\eta_A}{\rho_A}\right]$$

or by

$$D = \epsilon[FL_B\bar{c}_B + (1 - F)L_A\bar{c}_A],$$

in which ϵ is a numerical factor whose value is between 1.000 and 1.200 on various assumptions, F is the mol fraction of A, η and ρ are the viscosities and densities of the two gases involved, while L_A, L_B and $\bar{c}_A$, $\bar{c}_B$ are the mean free paths and average

thermal velocities. Thus the theory predicts, for a given value of F, that the diffusivity should vary with temperature and pressure in the same way as do the ratios $\frac{\eta}{\rho}$ for the two gases. Since L_A and L_B are proportional to $\frac{1}{p}$, and to T *at constant pressure*, and $\bar{c}_A$ and $\bar{c}_B$ are proportional to $\sqrt{T}$, D should be proportional to the $3/2$ power of the absolute temperature, and inversely proportional to the pressure. The accuracy of the measurements in this field is not so great as for the related effects of viscosity and heat conduction. From the experimental results, taken at pressures around atmospheric and at temperatures near normal room temperatures, it can be said that the diffusivity varies inversely as the pressure and as a power of the absolute temperature between 1.75 and 2.

In the discussion of viscosity it was seen that η, by the simple theory, varied as $T^{1/2}$ and not at all with p. Moreover, if the perfect gas laws are applicable, ρ varies as T^{-1} at constant pressure and as p. Putting these together, one has that on simple theory the diffusivity should vary as $T^{3/2}$ and as p^{-1}. The observed exponent for the variation is somewhat greater, as was just stated, and this is consistent with the fact that η actually varies with T according to a higher power than $T^{1/2}$. This more rapid increase in the case of viscosity was explained by Sutherland (Sec. 62) in terms of the effect on the mean free paths of attracting forces between the molecules. A similar analysis might be developed for the theory of diffusion, but it should be observed that it would be more complicated owing to the necessity of taking into account the attraction of A molecules on each other; that of A molecules on B molecules, and finally of B molecules on each other.

The next point on which it is interesting to compare theory and experiment is that of the variation of the diffusivity with the composition of the gas mixture. According to the simple theory, there should be a linear dependence on the mol fraction which is rather large when the values of $L\bar{c}$ for the two gases are quite different. On the other hand, according to a kinetic theory of diffusion developed by Stefan[11] and Maxwell, for which there is no space here, the result is obtained that the diffusion should be independent of the composition and that the value should be

$$D = 1.336\frac{\eta}{\rho}$$

(see Jeans, p. 317).

The investigation of the dependence of D on composition was made the subject of a series of doctors' dissertations by R. Schmidt (1904), O. Jackmann (1906), R. Deutsch (1907), and A. Lonius (1909), at Halle. The results of all this work are summarized in a paper by Lonius.[12] The following table, from this paper, summarizes the results:

DEPENDENCE OF D ON COMPOSITION

Gases		F	D	Observer
A	B			
O_2	H_2	0.5	0.27335	Jackmann
		0.252	0.27609	Jackmann
N_2	H_2	0.5	0.26565	Jackmann
		0.235	0.26830	Jackmann
O_2	N_2	0.5	0.073035	Jackmann
		0.467	0.073332	Jackmann
O_2	H_2	0.25	0.27616	Deutsch
		0.5	0.28003	Deutsch
		0.75	0.28934	Deutsch
CO_2	H_2	0.25	0.21351	Deutsch
		0.5	0.21774	Deutsch
		0.75	0.22772	Deutsch
Ar	He	0.5	0.25405	Schmidt
		0.377	0.25040	Schmidt
Ar	He	0.273	0.24818	Lonuis
		0.315	0.24965	Lonuis
		0.677	0.25626	Lonuis
		0.763	0.26312	Lonuis

The conclusion reached from this program of experiments is that, while D varies with composition, in no case was the variation more than about 8 per cent of the mean value of D. The Stefan-Maxwell theory is therefore incomplete. The theory of inter-diffusion, or transfer theory, gives the correct sense of the variation with composition but predicts a much greater amount of variation than is actually observed.

The transfer theory of diffusion is brought more nearly into accord with experiment through the theoretical work of Jeans[7]

in applying a correction for persistence of velocities. The researches of Chapman[5] and Enskog[6] on diffusion by more rigorous mathematical methods lead to formulæ which predict the actual variation of D with composition quite closely. As a result of these more advanced developments of the theory it may be said that the experiments on this point are fully explained by the kinetic theory.

One more point remains on which comparison between theory and experiment may be made and that is as to the value of the factor ϵ, occurring in the equation

$$D = \epsilon\frac{\eta}{\rho},$$

in which D is the coefficient of diffusion of the gas into itself. Although this quantity cannot be determined experimentally, a method has been indicated by Lord Kelvin[13] whereby it may be estimated from data on the diffusivity of various pairs of gases. From the measurements of Loschmidt on diffusion and the modern data on viscosity the following table was compiled:

Experimental Values of ϵ

Gas	D	ϵ (obs.)
H_2	1.31	1.37
O_2	0.189	1.40
CO	0.174	1.34
CO_2	0.109	1.50

It will be observed that all of these values lie between the extremes 1.200 for elastic spheres and 1.504 for molecules repelling according to the inverse fifth-power law.

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12. Lonius, A.: *Ann. Physik.*, **29**, 664, 1909. Chapman, *Phil. Trans.*, **A211**, 478, 1911.
13. Kelvin: "Baltimore Lectures," p. 295.

Books Recommended

a. Meyer, O. E.: "Kinetic Theory of Gases," translated by Baynes, Chaps. VII, VIII, IX; also Appendices IV, V, VI, Longmans, Green & Co., London, 1899.
b. Jeans, J. H.: *Loc. cit.*, Chaps. XI, XII, XIII. This book is excellent on this subject, giving excellent references with an admirable comparison of theory and experiment.
c. Jaeger, G.: Winklemann's "Handbuch der Physik," "Kinetic Theory of Gases," pp. 734, 753, vol. 3; Johann Ambrosius Barth, Leipzig, 1906.

CHAPTER VII

THE LAWS OF RAREFIED GASES AND SURFACE PHENOMENA

76. Introduction.—The study of this phase of the subject may be begun from the historical point of view. The early investigations of gaseous viscosity were carried out largely by means of the study of the flow of gases in capillary tubes. It was shown from a theoretical deduction of the coefficient of viscosity η (Sec. 60) that this coefficient of viscosity is independent of the gaseous pressure through wide ranges of pressure. It fails to do this at low pressures, however, and the failure was ascribed to the fact that, as the pressure decreases, the mean free path becomes comparable with the dimensions of the apparatus used. Thus the assumptions made involving the statistical conditions under which η is defined no longer hold, and the flow cannot be treated in the usual way. The point at which the breakdown of this phenomenon occurs, however, depends on the dimensions of the apparatus used and the nature of the measurement. Its discussion, therefore, requires that the deviation be studied from the point of view of some given process of measurement. Historically, this occurred in a study of the laws of flow of gases through a capillary tube. At high pressures, and even down to a few millimeters of pressure the law of Poisseuille[1] holds. As the mean free path of the molecules approaches the diameter of the tubes used, the law fails. The failure is in the sense as if, instead of the velocity of flow being zero at the walls (an assumption made in deducing Poisseuille's law and which this law justified), it has a value greater than 0; that is, the gas appears to slip past the wall. The amount of gas coming out from a tube under these conditions therefore appears to be greater than the diameter of the tube would warrant. The experiments of Kundt and Warburg[2] in 1875 showed that an extension of the law of flow was necessary at low pressures, and indicated how this should be done. Theoretically, the conditions determining the flow were worked out successfully by Maxwell[3] for this case in

1879. The analysis of the failure of the law, however, remained incomplete until the measurements of Knudsen[4] in 1908 threw more light on it. It thus became possible to explain the phenomenon fairly completely. The further researches of Knudsen on this and other low-pressure phenomena following the work mentioned directed attention to the possibilities of a successful treatment of such problems by kinetic-theory methods. It also led, together with the development of more powerful pumps, to a study of methods of low-pressure measurements. With the impetus given by these investigations, the theory of heat conduction in a gas at low pressures and the heat transfer from solid surfaces to gases at these pressures were carried on. Another phenomenon was also discovered and studied at low pressures. This is known as thermal transpiration. It consists of the flow of gas from a *cooler* rarefied body to a *hotter* one when these are connected by a capillary tube. In the development of the theory of heat conduction in a rarefied gas, together with the development of pressure-measuring devices, another set of phenomena received a study and some clarification. These are the so-called radiometric phenomena. The Crookes radiometer, so often seen in opticians' windows, consisting of a set of mica vanes blackened on one face and mounted on an axis so that they are free to rotate inside a partially evacuated glass vessel and which rotate when radiation falls on them, is a good example of this type of phenomena. The action of various types of instruments showing such effects have been quite recently studied from the standpoint of low-pressure conditions and have in some cases received a satisfactory explanation.

All these phenomena at low pressures in contradistinction to high-pressure phenomena emphasize the importance of impacts between molecules and the walls of the vessel relative to the intermolecular impacts so prominent at higher pressures. This has two effects: The first is to make the various phenomena observed much more a characteristic effect of the particular apparatus and experimental arrangement, thus making generalization partially impossible and conclusions drawn from observations apparently contradictory. The second effect is that it becomes necessary, to scrutinize, from the kinetic point of view, the nature of the momentum or energy exchange involved in collisions between gaseous molecules and solid surfaces. For instance, as will be seen in the discussion of capillary flow at low

pressures, the question arises as to whether the impinging molecules suffer specular reflection from the walls or whether they are reflected from the walls with a random distribution of velocities. Again, when molecules of one temperature strike a surface at another temperature one might well ask if the recoiling molecule left with the temperature of the surface or with a temperature intermediate between the two. This leads, therefore, to the study of the reflections of gas molecules from surfaces in general. The interpretations of the results of various observers lead to slightly differing answers to these questions, and at present there is no general completely satisfactory theory. It is possible that the different conditions actually lead to different processes of reflection, or, as stated above, the particular nature of the apparatus in each set of observations gives results so characteristic of the apparatus and conditions used that it is impossible to single out the true interpretation as regards the question of reflection.

Intimately connected with the question of reflection comes a question raised by the fact that a considerable proportion of the molecules appear to leave the solid surface with a random distribution of velocities. Overlooking the molecular roughness of the surfaces some observers are constrained to believe that the molecules actually condense on the solid surfaces and remain there for a period of time long compared to the time of a molecular gas impact. Thus the question of the formation of layers of gas molecules on surfaces, or perhaps, more generally, the question of "sorption" of gas molecules, is brought up. Outside of the possibility of the actual solution of the gas in the solid, true *absorption* (*e.g.*, the case of H_2 in Pd metal, or of H_2O in glass), two other types of surface absorption are shown to exist by Langmuir.[5] These are the *adsorbed* monomolecular layers of gas molecules, a reversible phenomenon (whose equilibrium is governed by temperature), and a chemical type of adsorption which depends on primary chemical valence forces. The latter type of adsorption is of great importance in phenomena of surface catalysis of chemical reactions.

In this chapter the subject of low-pressure phenomena will be introduced with a derivation of Poisseuille's law for capillary flow at high pressures, as this gives a clear and logical introduction to surface effects. The extension of this by Maxwell to low pressures will then be given, introducing Maxwell's assumptions. Then will follow Knudsen's contributions to the experimental

and theoretical sides of this question and a discussion of the effusion of gases at low pressures. Following this a section will be devoted to some of the questions of heat conduction at low pressures and the heat transfer to solid surfaces. The theory of the molecular manometer of Knudsen and the problems of thermal transpiration will follow in the next sections. Following this there will be a brief discussion of repulsion radiometers, including the Crookes radiometer. In the succeeding section a summary of the question of molecular reflection from solid surfaces will be given together with a brief discussion of sorption, with special emphasis on Langmuir's work on adsorption. It may be added that an excellent resumé of some of this work was written by Dunnoyer[6] in a small booklet of the series issued by the Sociètè Française de Physique, Series 2, page 214, published by Gauthier Villars, Paris, 1913.

77. Deduction of Poisseuille's Law of Flow of Gases through a Capillary Tube, and the Definition of the Coefficient of Slip.—

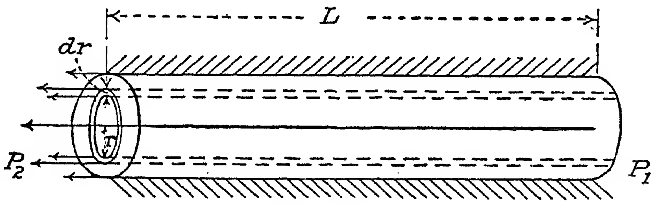

FIG. 42.

Assume a section of a capillary tube down which a gas is flowing as the result of a pressure difference $p_1 - p_2$ at its two ends. Take a small cylindrical section δr at a distance r from the axis of the tube (Fig. 42). The force F_1 acting on this is given by $2\pi r \delta r$-$(p_1 - p_2) = F_1$. If the flow has reached a steady state, equilibrium exists between this force and the forces of viscous drag acting across the boundaries of the surfaces, $2\pi rL$ and $2\pi(r + \delta r)L$ of the section, where L is its length. The force F_2 on these surfaces is composed of two components. The first component F_{2i} is that of the inner faster layer of gas and is given by an equation of the form $F = \eta S\dfrac{dv}{dr}$ by the definition of viscous drag, where S is the area of the cylindrical surface, η the coefficient of viscosity, and $\dfrac{dv}{dr}$ is the velocity gradient. As $\dfrac{dv}{dr}$ is negative, for v decreases as r increases, and as $S = 2\pi rL$, $F_{2i} =$

$-2\pi\eta rL\frac{dv}{dr}$. The second component F_{2o} is the drag produced by the slower outer layer of gas of surface $S = 2\pi(r + dr)L$. As here the gradient of velocity is $-\frac{d\left(v + \frac{dv}{dr}\delta r\right)}{dr}$ the force F_{2o} is,

$F_{2o} = -2\pi\eta(r + \delta r)L\frac{d\left(v + \frac{dv}{dr}\delta r\right)}{dr}$. Now $F_2 = F_{2o} - F_{2i}$, and for equilibrium $F_1 = F_2 = F_{2o} - F_{2i}$. One therefore has for the differential equation of flow

$$2\pi r(p_1 - p_2)\delta r = -2\pi\eta(r + \delta r)L\frac{d\left(v + \frac{dv}{dr}\delta r\right)}{dr} + 2\pi\eta rL\frac{dv}{dr}.$$

Canceling common terms and reducing the equations,

$$(p_1 - p_2)r = -\eta L\left(r\frac{d^2v}{dr^2} + \frac{dv}{dr}\right)$$

if one neglect the term $-\eta L\frac{d^2v}{dr^2}\delta r^2$, which is an infinitesimal of the second order. Hence

$$-\frac{p_1 - p_2}{\eta L} = \frac{d^2v}{dr^2} + \frac{1}{r}\frac{dv}{dr}.$$

Since $\frac{p_1 - p_2}{\eta L}$ is a constant of the apparatus, $\frac{d^2v}{dr^2}$ and $\frac{1}{r}\frac{dv}{dr}$ are both constant. A particular solution* of such an equation will take the form $v = A + Br^2$, where A and B are constants to be determined. Now

$$\frac{dv}{dr} = 2Br \qquad \frac{1}{r}\frac{dv}{dr} = 2B$$

$$\frac{d^2v}{dr^2} = 2B, \text{ thus } 4B = -\frac{p_1 - p_2}{\eta L},$$

whence

$$v = A - \frac{p_1 - p_2}{4\eta L}r^2.$$

* The solution of the differential equation above can, of course, be undertaken by more general methods. The general solution does not differ from the one above except for the presence of an exponential term which vanishes when the boundary conditions are fulfilled. The method of solution outlined above is simpler than the rigorous solution and so is given at this point.

If $v = 0$ when $r = R$, where R is the radius of the tube, *there is no slip* at the surface of the tube and the equation yields $0 = A - \frac{p_1 - p_2}{4\eta L}R^2$, whence $A = \frac{p_1 - p_2}{4\eta L}R^2$.

Thus the layer δr at a distance r from the axis of the tube has a velocity v given by

$$v = \frac{(p_1 - p_2)}{4\eta L}(R^2 - r^2).$$

To get the volume V of gas flowing out of the tube per second it is necessary to integrate $v(2\pi r dr)$, the volume flowing out of a layer dr from $r = 0$ to $r = R$, the radius of the tube.

$$\begin{aligned} V &= \int_0^R 2\pi r \frac{(p_1 - p_2)}{4\pi\eta L}(R^2 - r^2)dr \\ &= \frac{\pi(p_1 - p_2)R^4}{8\eta L}. \end{aligned}$$

If L is short, a correction should be made for the turbulent flow at the orifices. For sufficiently long tubes the law holds well, the length necessary for this depending on the value of R. Again, as was stated in the preceding section, when the pressures are low or when $p_1 - p_2$ is very great the law fails, for then v is not 0 when $r = R$. That is, the gas slips past the walls with a velocity v_0 at the walls.

To take care of slip at the walls it must be remembered that the assumption that $v = 0$ when $r = R$ was made in order to determine A. In order to handle the case when $v = v_0$ at $r = R$ it becomes necessary to assume that at $r = R$ there is a frictional force f on the surface of the gas at the tube wall. This force f may be written $f = \epsilon S v_0$; where $S = 2\pi RL$, v_0 is the velocity of the gas at $r = R$, and ϵ is a numerical coefficient of the force. The force at the boundary due to its drag is therefore proportional to the velocity and the surface, while its magnitude is controlled by these and a numerical coefficient of considerable theoretical interest. With these assumptions the condition for equilibrium at the wall (*i.e.*, when $r = R$) will be given by the following equation:

$$2\pi R\delta r(p_1 - p_2) = f - \left(-2\pi RL\eta\frac{dv}{dr}\right),$$

where the first term is the force F_1 due to the pressure on the layer δr at $r = R$, f is F_{2o}, which is now the drag due to the walls,

and $-2\pi RL\eta\frac{dv}{dr}$ is F_{2i}, the drag of the inner gas on the gas at the surface. If the layer δr be taken sufficiently small, the term $2\pi R\delta r(p_1 - p_2)$ becomes 0. Thus

$$-2\pi R\eta L\frac{dv}{dr} = f = 2\pi RL\epsilon v_0, \quad \text{or} \quad v_0 = -\frac{\eta}{\epsilon}\frac{dv}{dr}.$$

But in the preceding analysis

$$\frac{dv}{dr} = -\frac{1}{2}\frac{p_1 - p_2}{\eta L}r,$$

whence

$$v_0 = \frac{r}{\epsilon}\frac{p_1 - p_2}{2L}.$$

Putting in this expression for $v = v_0 = \frac{r}{\epsilon}\frac{p_1 - p_2}{2L}$ at $r = R$, one has to determine A by

$$v_0 = A - \frac{p_1 - p_2}{4\eta L}R^2 = \frac{R}{\epsilon}\frac{(p_1 - p_2)}{2L},$$

or

$$A = \frac{(p_1 - p_2)}{4\eta L}\left(R^2 + \frac{2R\eta}{\epsilon}\right).$$

This yields for v, the velocity at r, the expression

$$v = \frac{(p_1 - p_2)}{4\eta L}\left(R^2 - r^2 + 2R\frac{\eta}{\epsilon}\right),$$

and for the volume of gas flowing out per second the expression

$$V = \frac{\pi(p_1 - p_2)}{8\eta L}\left(R^4 + \frac{4\eta}{\epsilon}R^3\right).$$

Here ϵ is a constant of the walls and the gas. This equation shows that when measurements are made roughly the slip at the walls may be neglected. The deviation from the first equation deduced may be seen at once from

$$V = \frac{\pi(p_1 - p_2)}{8\eta L}R^4\left(1 + \frac{4\eta}{\epsilon R}\right).$$

It depends on R. If R is large compared to $\frac{4\eta}{\epsilon}$, it can be neglected.

The ratio $\frac{\eta}{\epsilon}$ which determines the question of the importance of this term in the theory is called the "coefficient of slip" and is

designated symbolically by $\zeta = \frac{\eta}{\epsilon}$. It really gives the ratio of the internal friction of the gas (*i.e.*, the coefficient of the viscosity) to the coefficient of external friction against the walls. The value of ϵ, and consequently of ζ, must depend on the nature of the impacts which are assumed between the gas and the walls. It is therefore necessary to derive an expression for this quantity in terms of the kinetic theory before proceeding further. The relation to be considered is due to Maxwell and its detailed consideration cannot find place here. The ideas used, however, will be developed at this point, together with the result.

If the surface were perfectly smooth, specular or perfect reflection would be observed, that is, the molecules striking the surface at any angle ϕ (Fig. 43) would rebound, conserving the velocity

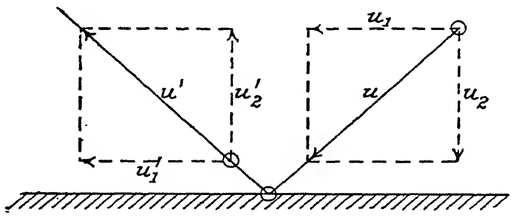

FIG. 43.

parallel to the surface, but having the component of velocity perpendicular to the surface reversed. With such reflection the only force on the wall would be the pressure normal to it. The velocity at the surface would then be the velocity of flow along the wall (*i.e.*, there would be no drag, ϵ would be 0, and the gas would flow down the tube with no action on the walls), that is, its velocity through the cross-section of the tube would be uniform. This is not the case, for actually there is a frictional term. This means that there must be some mechanism by which the gas is retarded by the walls. If the walls were composed of spherical gas molecules at rest with large spaces between them, the molecules striking such a wall would lose their momentum, for, on the average, they would be reflected as if they had velocities after reflection equally probable in all directions. Maxwell points out that such molecules could be considered as "*absorbed and reevaporated*" from the surface at a temperature corresponding to that of the gas, if the wall and the gas are at the same temperature. With such a process occurring, the gas would still have a velocity of slip. In this case, however, the velocity at the wall

would be less than that in the center and the gradient could be calculated. How this occurs can easily be seen. The molecules leaving the surface must equal those approaching it when equilibrium has set in. Those leaving have random velocities, and hence no streaming velocity down the tube. Those approaching the walls have an average velocity component v appropriate to the scenes of their last impacts in the gas. Thus the layer of gas nearest the wall is composed, on the average, of equal numbers of molecules with zero streaming velocity and with an average velocity v. There will thus be a velocity jump at the surface equivalent to $\frac{v}{2}$. If the molecules of the wall are not distributed as assumed by Maxwell, they may partly specularly reflect the impinging molecules. In such a case the slip will be greater than that above, and v_0 will be increased. Actually, the surface molecules of the solid are not necessarily distributed to give diffuse reflection, but, as Maxwell points out, they act so as to shield each other from direct impacts of gas molecules. The result will be that very oblique impacts will cause reflection from the outer ends of the wall molecules. They will thus be more nearly specularly reflected than will the molecules striking normally. The outcome of this will be that there will be a slip in the gas which will depend on the relative importance of the two kinds of reflection. To study this, he assumes that those molecules striking a fraction f of the surface will be absorbed, and $1 - f$ will be specularly reflected. To calculate the slip he then proceeds as follows: Assume the gas to be flowing along y past a plane surface yz, and that the positive x direction is the direction of the gas from the wall. Call u, v, and w the components of velocity along the three axes. If, now, a particular velocity be chosen one may term $-u_1$ the incident value of the x component, and $+u_2$ as the rebounding value of the x component of the molecules that are specularly reflected. The x component of the evaporated molecules will be $+u'$. The mass of gas of velocity component $-u_1$ incident on unit surface of the plane per unit time is, then, $-\rho_1 u_1$, where ρ_1 is the density of molecules of velocity component u_1 in the gas. Of these molecules the fraction $1 - f$ has u reversed in direction. For the fraction f evaporated, the average component of velocity is u', corresponding to the temperature Θ' of the wall. With these considerations one may write that for the fraction f that are absorbed the

momentum normal to the surface must equal the momentum of the same molecules reevaporated from the surface at the same temperature, that is,

$$-f\rho_1 u_1 = f\rho_2' u_2'.$$

It also follows that the total momentum given to the wall by the molecules leaving is expressed by

$$\rho_2 u_2 = -(1 - f)\rho_1 u_1 + f\rho_2' u_2',$$

where ρ_1, ρ_2, and ρ_2' are the densities of the molecules having velocities u_1, u_2, and u_2'.

Along the direction of motion y the velocity is v, and the incident momentum is $\rho_1 u_1$, the mass striking per unit time times the incident velocity v. Of these, $1 - f$ are specularly reflected and $(1 - f)\rho_1 u_1 v_1$ is the momentum along the wall which is not changed, that is, this is the momentum exchange which causes the additional slip. The momentum of the evaporated portion along y which has an average velocity component $-v$ (the relative velocity between gas and the surface) is, then, $-f\rho_2' u_2' v$. The expression for the momentum of the reflected molecules along y is, then, expressed by the relation

$$\rho_2 u_2 v_2 = (f - 1)\rho_1 u_1 v_1 - f\rho_2' u_2' v.$$

Between this and the preceding equations the quantities $f\rho_2' u_2'$ can be eliminated and one has for the momentum transfer the following equation:

$$(1 - f)\rho_1 u_1 v_1 + \rho_2 u_2 v_2 + v[(1 - f)\rho_1 u_1 + \rho_2 u_2] = 0.$$

To solve this in order to get the velocity of the gas along the wall, the appropriate values for ρ_1, ρ_2, u_1, u_2, and v_1, v_2, and v must be put into the equation, and integrated for u from $-\infty$ to 0 and with respect to v and w from $-\infty$ to $+\infty$, and for the molecules which are leaving the surface for u from 0 to ∞. The functions to be inserted are taken from a more general expression deduced by Maxwell for the case where the temperatures of the wall and gas may be different. They are too lengthy to include in this place. With certain simplifications to facilitate solution and the assumption that the temperatures of the gas and the wall are the same, he finds that the velocity of the gas at the wall is given by

$$v_0 = \sqrt{\frac{\pi}{2}}\,\eta\sqrt{\frac{1}{p\rho}}\left(\frac{2 - f}{f}\right)\frac{dv}{dx},$$

where $\frac{dv}{dx}$ is the gradient of velocity normal to the wall. It is seen that when $f = 1$, $v_0 = \sqrt{\frac{\pi}{2}}\,\eta\sqrt{\frac{1}{p\rho}}\,\frac{dv}{dx}$, a minimum value, and as f decreases v_0 rapidly increases. For the case of the flow in a tube $\frac{dv}{dx}$ is replaced by the $\frac{dv}{dr}$ above, and one has

$$v_0 = \frac{\eta}{p}\sqrt{\frac{\pi}{2}\frac{RT}{M}}\left(\frac{2-f}{f}\right)\frac{dv}{dr},$$

where M is the mass of a gram-molecule, R is the gas constant per gram molecule, and T is the absolute temperature. But it was found in deducing the slip term of Poisseuille's equation that

$$v_0 = +\frac{\eta}{\epsilon}\frac{dv}{dr} = \zeta\frac{dv}{dr},$$

whence

$$\zeta = \frac{\eta}{\epsilon} = \frac{\eta}{p}\sqrt{\frac{\pi}{2}\frac{RT}{M}}\left(\frac{2-f}{f}\right).$$

This at once gives the value of the coefficient of slip ζ in terms of the fraction f of the molecules evaporated from the surface, or the fraction $1 - f$ specularly reflected. It is thus seen that the term $\zeta = \frac{\eta}{\epsilon}$ in Poisseuille's law depends on the $\sqrt{T}$, on f, and on $\frac{1}{p}$. It is the variation of $\frac{\eta}{\epsilon}$ with pressure that is of interest, for the correction term for slip in Poisseuille's law depends on $\left(1 + \frac{4\eta}{\epsilon R}\right)$. As long as pR is large compared with the other quantities, the term may be neglected, but when p becomes small the correction must be added. One is now in a position to compare the theory with experiment.

Before doing this it might be stated that Baule[7] also found an expression for the coefficient of slip similar to that of Maxwell to a first approximation. Baule interprets f in terms of a coefficient which gives the fraction of molecules which make only one impact with the walls of the solid. Thus such molecules do not come into complete equilibrium with the walls, and retain some of their incident velocity. Those that escape after several impacts have the random distribution of evaporated molecules of Maxwell. If $f = 1$, his formula becomes identical with Maxwell's. It

merely makes a more accurately analytical picture of what takes place at the wall. A very accurate measurement of the coefficient of slip was made by Blankenstein.[8] He used the rotating-cylinder method (see Sec. 63) in the gases H_2, He, air, and O_2 where the gases were kept very pure by a constant-flow method at low pressures. The surfaces were burnished surfaces of silver oxide deposited on brass. In this method the deflection is related to the momentum transfer of the gas by the factor $\eta\left(\frac{V}{d}\right)$ at high pressures. Here $\frac{V}{d}$ is the velocity gradient at the surface, d being the separation of the cylinders and V the velocity of the moving cylinder. If slip appears, the momentum transfer is lessened and it may be written as $\frac{\eta V}{(d + 2\zeta)}$, where ζ is the coefficient of slip defined above. By measuring the deflection of the cylinder at higher pressures and again at pressures where slip occurs, it should be less at the low pressures in the ratio $\frac{d}{(d + 2\zeta)}$. By measuring this difference at different low pressures, ζ may be computed as a function of p. From the values of ζ and p it is possible to determine f. For the gases He, H_2, air, and O_2 the values of f obtained were 1.00, 1.00, 0.98, and 0.99 respectively. Thus it might be concluded that there is practically no specular reflection for H_2 and He, while air and O_2 show about 1 or 2 per cent of slip. Other experiments by Van Dyke[9] and Stacy,[10] using shellac and oil surfaces with gases of a more doubtful purity, gave a specular reflection of from 8 to 20 per cent. The question of such reflection will, however, be more properly treated later on. The verification of Maxwell's equation, no matter what the theoretical basis of f, places this mode of procedure as a legitimate one. It is thus permissible to consider the apparent change in the outflow from a tube as pressure decreases, found by Kundt and Warburg,[2] from this point of view. The equation for the volume of gas flowing out of a tube as a function of the various quantities entering in was given as

$$V = \frac{\pi(p_1 - p_2)}{8\eta L} R^4\left(1 + \frac{4\eta}{\epsilon R}\right).$$

This can be changed to the mass of gas G flowing out in unit time, which is what is actually measured. As $p = \frac{1}{3}\rho C^2$, where ρ is the

density, and as $\frac{1}{3}mN_AC^2 = \frac{1}{3}MC^2 = RT$, where M is the mass of a gram-molecule, therefore $\rho = \frac{pM}{RT}$. Since $G = V\rho$, the equation for G becomes

$$G = \frac{\pi R^4}{8\eta L}(p_1 - p_2)\frac{M}{RT}p\left(1 + 4\zeta\frac{1}{R}\right).$$

Thus G plotted as ordinates against p as abscissæ is a straight line that should pass through the origin. As the pressure becomes very low, the factor $\left(1 + \frac{4\zeta}{R}\right)$ becomes appreciable, for ζ is proportional to $\frac{1}{p}$, as shown by Maxwell's theory. This causes G to decrease more slowly as p decreases, for the ζ which increases as p decreases counteracts the effect of pressure in decreasing G. This portion of the curve was that studied by Kundt and Warburg and it is explained by slip.

As the pressures decrease still more, the flow at first rises as pressure decreases and finally ceases to change with pressure at all, remaining constant. It was the portion of the curve for G, just before the rise and from there on, for which the theory was incomplete and was extended by the work of Knudsen[11] in 1909.

78. Flow in Tubes for Rarefied Gases, Knudsen's Equation.—The constant régime sets in when the pressures are so low that the mean free path of the gas molecules is comparable with R. If this occurs one cannot speak of a flow in the ordinary sense at all. It is perhaps best to discuss and interpret the régime of constant outflow first, for the transition from the Kundt and Warburg deviation from the straight line to the constant outflow through the minimum marks a transition from one type of mechanism of flow to the other which cannot be clearly grasped until the initial and final conditions of flow are understood.

The derivation of the equation for this régime, due initially to Knudsen, is very instructive. He starts with the assumption that the number of molecules striking a cm² of surface per second is $\frac{1}{4}N\bar{c}$ (see Secs. 40 and 71), where $\bar{c}$ is the average velocity of the molecules. If there are N molecules per cm³, the number dN with velocity components between c and $c + dc$ is given by the Maxwell distribution law as

$$dN = \frac{4N}{\alpha^3\sqrt{\pi}}c^2e^{-\frac{c^2}{\alpha^2}}dc,$$

where α is the most probable speed. The number of these molecules which strike 1 cm^2 of surface per second is, then, $\frac{1}{4}cdN$. Since the molecules which have a component of velocity of translation ω parallel to the wall on striking are absorbed, and reemitted equally in all directions (that is, with the f of Maxwell equal to 1), the momentum given the wall by these dN molecules is $\frac{1}{4}cm\omega dN$. Since ω is the component of the velocity of the gas molecules parallel to the wall, ω may be written kc where k is a constant of proportionality. This merely expresses ω as a fractional part of c, the molecular velocity, and ascribes the Maxwell distribution to the components ω in this manner. The momentum transfer is, therefore, $\frac{1}{4}kc^2mdN$. The momentum B given the wall by molecules of all velocities is therefore given by

$$B = \frac{1}{4}Nk\frac{4}{\sqrt{\pi}}m\int_0^\infty \frac{c^4}{\alpha^3}e^{-\frac{c^2}{\alpha^2}}dc = \frac{1}{4}Nkm\frac{3}{2}\alpha^2.$$

Substituting $\bar{c}$ for α, where $\bar{c} = \frac{2\alpha}{\sqrt{\pi}}$, one gets $B = \frac{3\pi}{32}Nmk\bar{c}^2$.

As $\bar{c}$ is $\frac{\Sigma\bar{c}}{N}$, therefore $k\bar{c} = \frac{\Sigma k\bar{c}}{N} = \frac{\Sigma\omega}{N} = v$.

This v is the geometric mean of the velocity of all molecules. It is therefore the velocity of the mass of gas down the tube, and one has $B = \frac{3\pi}{32}Nm\bar{c}v$. This assumes v constant across the tube. This assumption only holds, in the Knudsen régime, where the free path is great compared to the radius of the tube, and hence there is no velocity gradient normal to the walls. Physically, this means that the gas is so rarefied that the velocity transition at the surface which was confined to a narrow region originally now extends across the whole tube.

For a tube of approximately cylindrical form, call dl the element of length of the tube, O its circumference at dl, and A its area of cross-section. In dt sec. this tube receives an amount of momentum given by $\frac{3\pi}{32}Nm\bar{c}vOdldt$. Setting $Nm = \rho$, the density of the gas, and expressing $\bar{c}$ in terms of the pressure p,

from the relation $p = \frac{\pi}{8}Nm\bar{c}^2$, the above quantity becomes

$$\frac{3}{8}\sqrt{\frac{\pi}{2}}\,\rho\sqrt{\frac{p}{\rho}}\,vOdldt.$$

If it is assumed that the wall Odl gets the whole momentum which results from the pressure drop $-\left(\frac{dp}{dl}\right)dl$ (that is, neglecting the end effects of the tube), one obtains the relation between the momentum transfer $-A\left(\frac{dp}{dl}\right)dldt$ in the time dt due to the pressure difference across the area A, and the momentum transfer to the wall as

$$\frac{3}{8}\sqrt{\frac{\pi}{2}}\,\rho\sqrt{\frac{p}{\rho}}\,vO = -A\frac{dp}{dl}.$$

For the mass G which goes through the area per second one can write $G = A\rho v$, whence

$$G = -\frac{8}{3}\sqrt{\frac{2}{\pi}}\sqrt{\frac{\rho}{p}}\,\frac{A^2}{O}\frac{dp}{dl}.$$

If the ratio of the density and pressure, when the pressure is in dynes per cm², is called ρ_1; then

$$G = -\frac{8}{3}\sqrt{\frac{2}{\pi}}\sqrt{\rho_1}\,\frac{A^2}{O}\frac{dp}{dl}.$$

If the volume of gas flowing through the tube be used instead of the mass of the gas, that is, if one write $Q_t = \frac{G}{\rho_1}$, then

$$Q_t = -\frac{8}{3}\sqrt{\frac{2}{\pi}}\,\frac{1}{\sqrt{\rho_1}}\,\frac{A^2}{O}\frac{dp}{dl}.$$

For steady flow, Q_t has the same value along the tube. Calling the length of the tube L and the pressure on its ends p_1 and p_2, $(p_1 > p_2)$, one obtains

$$Q_t\frac{O}{A^2}\,dl = -\frac{8}{3}\sqrt{\frac{2}{\pi}}\,\frac{1}{\sqrt{\rho_1}}\,dp,$$

which yields on integration

$$Q_t = \frac{1}{\sqrt{\rho_1}}\,\frac{(p_1 - p_2)}{\sqrt{\frac{3}{8}}\int_0^L \frac{O}{A^2}dl} = \frac{1}{\sqrt{\rho_1}}\,\frac{p_1 - p_2}{W},$$

that is,

$$Q_t = \frac{p_1 - p_2}{\sqrt{\rho_1}W},$$

where

$$W = \frac{3}{8}\sqrt{\frac{\pi}{2}}\int_0^L \frac{O}{A^2}dl.$$

W is a constant of the form and dimensions of the tube only. It has the same function as a resistance factor in electricity, and can be called the resistance of the tubes. Thus it is possible for this case of flow in tubes to carry over Kirchhoff's laws of branched circuits to the calculation of the gaseous flow in any system of tubes. For a cylindrical tube of radius R, $O = 2\pi R$ and $A = \pi R^2$, whence

$$W = \frac{3}{8}\sqrt{\frac{\pi}{2}}\frac{2}{\pi}\frac{L}{R^3},$$

and

$$Q_t = \frac{4}{3}\sqrt{2\pi}\frac{1}{\sqrt{\rho_1}}\frac{R^3}{L}(p_1 - p_2).$$

Where gases flow out of the ends of the tubes with a finite velocity, the whole pressure drop is not taken up in overcoming wall resistance, for the gas has a kinetic energy on leaving the tube which it got from the pressure difference. In this case the relation

$$\frac{3}{8}\sqrt{\frac{\pi}{2}}\rho\sqrt{\frac{p}{\rho}}\,vO = -A\frac{dp}{dl},$$

must be replaced by

$$\frac{3}{8}\sqrt{\frac{\pi}{2}}\,\rho\,\sqrt{\frac{p}{\rho}}\,vO = -A\frac{dp}{dl} - A\rho v\frac{dv}{dl},$$

where $G = A\rho v$ is the mass of the gas flowing out per second, and $\frac{dv}{dl}$ is the change in velocity per unit length of tube. Thus

$$\frac{3}{8}\sqrt{\frac{\pi}{2}}\frac{1}{\sqrt{\rho_1}}\frac{O}{A^2}G = -\frac{dp}{dl} - \frac{G^2}{A^2\rho_1}\frac{d}{dl}\left(\frac{1}{p}\right),$$

which on integration over the whole tube yields

$$\frac{3}{8}\sqrt{\frac{\pi}{2}}\frac{1}{\sqrt{\rho_1}}G\int_0^L \frac{O}{A^2}\,dl = p_1 - p_2 - \frac{G^2}{A^2\rho_1}\frac{p_1 - p_2}{p_1p_2}.$$

Again setting

$$W = \frac{3}{8}\sqrt{\frac{\pi}{2}}\int_0^L \frac{O}{A^2}\,dl,$$

then

$$G = (p_1 - p_2)\frac{\sqrt{\rho_1}}{W}\,\frac{1}{1 + \dfrac{G}{A^2\rho_1^{\frac{1}{2}}W}\,\dfrac{p_1 - p_2}{p_1p_2}}.$$

If the quantity

$$U = \frac{G}{A^2\rho_1^{\frac{1}{2}}W}\,\frac{p_1 - p_2}{p_1p_2}$$

is small compared to 1, one obtains the previous relation $G = \dfrac{\sqrt{\rho_1}}{W}(p_1 - p_2)$ and the quantity U becomes

$$U = \frac{1}{A^2W^2}\,\frac{(p_1 - p_2)^2}{p_1p_2}.$$

For a cylindrical tube this is

$$U = \frac{32}{9\pi}\,\frac{R^2}{L^2}\,\frac{(p_1 - p_2)^2}{p_1p_2}.$$

As U depends on $\dfrac{R}{L}$, it is seen that, for experimental cases where $\dfrac{R}{L}$ is of the order of $1/1000$, U must be much less than unity, even when p_1 is hundreds of times greater than p_2.

Thus the velocity of flow from a cylindrical tube at low pressures can be taken as

$$G = \frac{4}{3}\sqrt{2\pi}\sqrt{\rho_1}\,\frac{R^3}{L}(p_1 - p_2).$$

This differs materially from the Poisseuille's equation, having a coefficient of slip which reads

$$G = \frac{\pi R^4}{8\eta L}(p_1 - p_2)\,\frac{M}{R_0T}\left(1 + \frac{4\eta}{\epsilon}\,\frac{1}{R}\right)p.$$

The comparison is clearer if, for ρ_1, the quantity $\dfrac{\rho}{p}$ is used, for then

$$\frac{Nm}{\frac{1}{3}NmC^2} = \frac{\rho}{p} = \frac{N_Am}{R_0T} = \frac{M}{R_0T},$$

whence

$$G = \frac{4}{3}\sqrt{2\pi}\,\sqrt{\frac{M}{R_0T}}\,\frac{R^3}{L}(p_1 - p_2).$$

It is seen that for low pressures G is proportional to R^3, and not R^4 as in Poisseuille's law. Furthermore, G is independent of η and p.

The discussion of the minimum of the curves presupposes a comparison with the experimental results. In Figs. 44, 45*a*, and

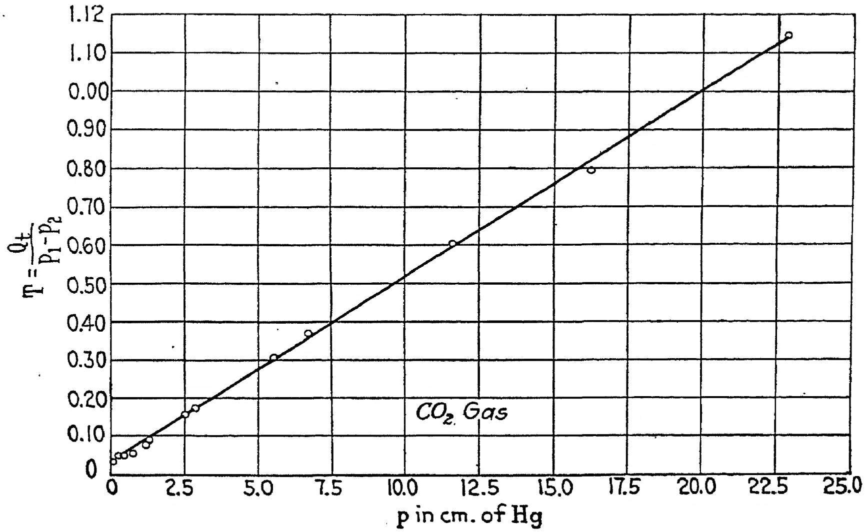

FIG. 44.

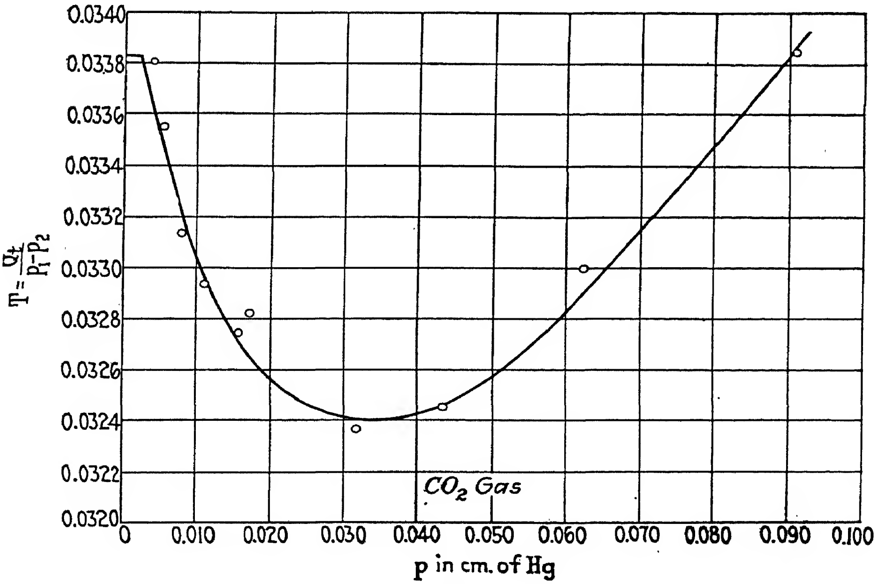

FIG. 45*a*.

45*b* the points found by Kundsen in CO_2 for a certain tube are given. In them $T = \dfrac{Q_t}{p_1 - p_2}$ is plotted against p in cm of mer-

cury. The régime from $p = 0.004$ cm to $p = 0.000011$ cm is shown in Fig. 45b on a logarithmic scale. As is seen at once, T decreases linearly with p from 22 to about 0.24 cm. From then

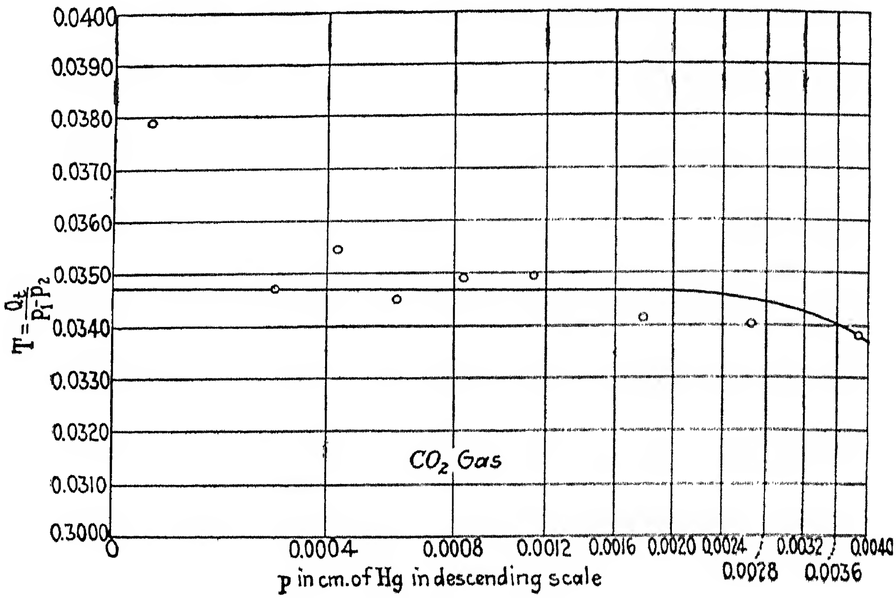

FIG. 45b.

on it falls to a minimum, rising again to $p = 0.0010$ cm, from which point on it remains as constant as the measurements will permit. The smooth curves which fit the results quite accurately are given by an empirical expression

$$T = ap + b\frac{1 + c_1 p}{1 + c_2 p},$$

where the constants a, b, c_1, and c_2 can be found from least-square reductions. These constants depend on the dimensions of the tube and other factors. All tubes used gave similar curves, the constants only differing. It is first necessary to correlate as many of the constants as possible with the constants deduced thus far from the theory. This is easily done for the constants a and b. The constants c_1 and c_2, however, are the ones related to the minimum of the curve. And it is their evaluation which will throw light on this process.

The constant a can be evaluated as follows. If Poisseuille's law is assumed to hold with no slip at the walls, it yields

$$T = \frac{\pi}{8}\frac{1}{\eta}\frac{R^4}{L}\,p.$$

This term is equivalent to the portion $T = ap$ of the empirical equation. The a should then be given by $a = \frac{\pi}{8}\frac{1}{\eta}\frac{R^4}{L}$. Calculating a for his tubes from this expression, Knudsen finds agreement with the observed values within the limits of experimental uncertainty.

For small values of p the equation goes over to the form $T = b$, for ap and $\frac{1 + c_1p}{1 + c_2p}$ become 0 and 1 respectively in this case. For the lowest pressures one has the conditions of molecular flow, in which $T = \frac{1}{W\sqrt{\rho_1}}$, and for cylindrical tubes of circular cross-section $T = \frac{4}{3}\sqrt{2\pi}\frac{1}{\sqrt{\rho_1}}\frac{R^3}{L}$. Hence b becomes $b = \frac{4}{3}\sqrt{2\pi}\frac{1}{\sqrt{\rho_1}}\frac{R^3}{L}$.

To obtain the values of c_1 and c_2, two cases must be considered. The first one is for pressures where the free path is small compared to the radius of the tube, but not negligibly small. The study of this case will give a ratio of the constants $\frac{c_1}{c_2}$. The second one is where the radius of the tube is smaller than the mean free path, but is not vanishingly small compared to this. The study of this condition leads to an evaluation of $c_2 - c_1$. The two cases together then afford means of obtaining c_1 and c_2.

For the first case p is so great that $\frac{1 + c_1p}{1 + c_2p}$ may be written as $\frac{c_1}{c_2}$. The equation then becomes $T = ap + b\frac{c_1}{c_2}$. Putting in the values of a and b one has that

$$T = \frac{\pi}{8}\frac{1}{\eta}\frac{R^4}{L}\,p\left(1 + \frac{32\sqrt{2}\,\eta}{3\sqrt{\pi}\sqrt{\rho_1}\,Rp}\frac{c_1}{c_2}\right).$$

But in this régime (which is that of Kundt and Warburg) Poisseuille's equation also holds, including the slip term. This law gives $T = \frac{\pi}{8}\frac{1}{\eta}\frac{R^4}{L}p\left(1 + \frac{4\zeta}{R}\right)$. Comparing the two expressions

for T, one has at once that $\zeta = \dfrac{8\sqrt{2}\eta c_1}{3\sqrt{\pi}\sqrt{\rho_1 p}c_2}$. The experiments of Kundt and Warburg showed that ζ was similar to the mean free path, so that ζ could be replaced by $k\lambda$, where k is a fraction nearly equal to 1 and λ is the mean free path. Also, since Maxwell's distribution law gives a relation between λ and η of the form

$$\lambda = \frac{\sqrt{\frac{8}{\pi}}\;\eta}{0.30967\;p\sqrt{\rho_1}},$$

then

$$\frac{k\sqrt{8}\eta}{\sqrt{\pi}(0.30967)\,p\sqrt{\rho_1}} = \frac{8\sqrt{2}\eta c_1}{3\sqrt{\pi}\sqrt{\rho_1 p}c_2},$$

that is, $\dfrac{c_1}{c_2} = 0.95k$. As k is less than unity, $\dfrac{c_1}{c_2}$ is a constant independent of the radius of the tube and the nature of the gas whose value is less than 0.95. In fact, Knudsen's experiments bear out the fact that $\dfrac{c_1}{c_2}$ is between 0.85 and 0.78 and is independent of tube radius, specific gravity, or viscosity of the gas, and he chooses $\dfrac{c_1}{c_2} = 0.81$.

The evaluation of $c_2 - c_1$ is a far more complicated question, for which there is not room in this text. The general considerations by which this end is reached are instructive, and may therefore be briefly indicated. At pressures where the free path is greater than the dimensions of the tube, but not much greater, both impacts with the walls and with other molecules occur. The momentum of the moving molecules can then be carried to the walls by two processes: either by direct impact with the walls, or by the molecules struck by these molecules, which therefore have some of the streaming motion. The former can be computed from the number of molecules striking unit area of the walls, which is $\dfrac{N\bar{c}}{4}$. The momentum carried by these two mechanisms can then be roughly evaluated. Allowance must be made in this calculation for the time elapsing between the impacts of the moving molecules and the others, and the transfer of this momentum to the walls. This calculation leads to the use of a

small numerical factor k of a value about $\frac{1}{2}$. Using this, T is calculated to be

$$T = \frac{4}{3}\sqrt{2\pi}\frac{1}{\sqrt{\rho_1}}\frac{R^3}{L}\left(1 - (1 - k)\frac{2R}{\lambda}\right)$$

for a cylindrical tube of circular cross-section. Comparison of this with the empirical equation, which for the approximate values of p for which this occurs takes on the form

$$T = ap + b(1 - (c_2 - c_1)\,p)$$

leads to the relation

$$(1 - k)\frac{2R}{\lambda} = \left(c_2 - c_1 - \frac{a}{b}\right)p.$$

This equation becomes

$$c_2 - c_1 = 1.2378\frac{R}{p\lambda} = 0.6117\frac{\sqrt{\rho_1}}{\eta}R.$$

in the event that $k = \frac{1}{2}$, if the values of a and b are substituted in it. The agreement is satisfactory in order of magnitude between the empirical $c_2 - c_1$ and the calculated $c_2 - c_1$. It indicates proportionality between $c_2 - c_1$ and $\frac{\sqrt{\rho_1}}{\eta R}$, but does not agree completely with the numerical factor for which Knudsen substitutes a value d. From the value for $\frac{c_1}{c_2}$ and the value for $c_2 - c_1$ containing d Knudsen deduces the values of c_2 and c_1, as

$$c_2 = d\frac{\sqrt{\rho_1}}{\eta}R$$

$$c_1 = 0.810d\frac{\sqrt{\rho_1}}{\eta}R,$$

$$T = \frac{\pi}{8}\frac{1}{\eta}\frac{R^4}{L}p + \frac{4}{3}\sqrt{2\pi}\frac{1}{\sqrt{\rho_1}}\frac{R^3}{L}\left(\frac{1 + 0.81d\frac{\sqrt{\rho_1}}{\eta}Rp}{1 + d\frac{\sqrt{\rho_1}}{\eta}Rp}\right).$$

This equation is now no longer completely empirical in the sense that all the constants are more or less rigorously deduced from theoretical considerations and are in no sense arbitrary. The only one approaching an arbitrary value is the constant d. Its numerical value was estimated from rough theoretical considerations only and hence is uncertain.

To obtain a more correct empirical value of d and to test the equation, the expression for T can be differentiated to find the value of p for the minimum of the curve. This leads to the expression for p_m, the pressure at the minimum:

$$p_m = \frac{\eta}{d\sqrt{\rho_1}R}\left(\sqrt{\frac{d - 0.190}{m}} - 1\right) = \frac{1}{c_2}\left(\sqrt{\frac{d - 0.19}{m}} - 1\right),$$

where $m = \frac{3\sqrt{\pi}}{32\sqrt{2}}$. From this it can be shown that the following conditions must hold. They are that

$$p_m c_2 = \text{constant.}$$

$$\frac{T_m}{T_0} = \text{constant } (T_0 \text{ is the value of } T \text{ when } p = 0).$$

$$\frac{R}{\lambda_m} = \text{constant.}$$

These conditions are tested on the empirical constants of his observations and found to hold. From the relation that $p_m c_2$ is a constant observed to be near unity, d is computed as 2.47. This value is checked by calculating $\frac{T_m}{T_0}$ and $\frac{R}{\lambda_m}$, using d from his equation for the minimum and comparing these with the observed values. They agree fairly well. If, then, these values be assumed, T, the outflow per unit pressure difference, is obtained as

$$T = \frac{\pi}{8}\frac{1}{\eta}\frac{R^4}{L}p + \frac{4}{3}\sqrt{2\pi}\frac{1}{\sqrt{\rho_1}}\frac{R^3}{L}\left(\frac{1 + 2.00\frac{\sqrt{\rho_1}Rp}{\eta}}{1 + 2.47\frac{\sqrt{\rho_1}Rp}{\eta}}\right)$$

or, expressed in terms of the mean free path,

$$T = \frac{Q_t}{p_1 - p_2} = \frac{\pi\sqrt{\pi}}{8\sqrt{8}(0.30967)}\frac{R^4}{L}\frac{1}{\lambda\sqrt{\rho_1}} + \frac{4}{3}\sqrt{2\pi}\frac{R^3}{L}\frac{1}{\sqrt{\rho_1}}\left(\frac{1 + 0.81\frac{5R}{\lambda}}{1 + \frac{5R}{\lambda}}\right).$$

Thus, with the aid of the kinetic-theory analysis at low pressures, one has a complete analysis of the flow of gases down a tube of cylindrical cross-section. In making this analysis, certain new concepts about the momentum exchanges between solid surfaces and the gas have also been derived.

79. The Effusion of Gases.[12]—Another effect which is closely related to the above phenomenon is that of the effusion of gases through small openings. In the last section the laws of flow of gases through tubes of finite length at low pressures were discussed. If, now, the tube be considered infinitely short, there is the phenomenon of the effusion of gases.

Picture two vessels A and B having N' and N'' molecules per cm³ in each. If the two are connected by a hole of area s in an infinitely thin partition, then molecules strike the opening from the sides of A and B in different numbers. The number of molecules striking s per second from the side A will be $\frac{N'\bar{c}}{4}s$, and the number striking it from the side of B per second will be $\frac{N''\bar{c}}{4}s$, where $\bar{c}$ is the average velocity of the molecules. As a result, there will be a number $n = \frac{1}{4}\bar{c}s(N' - N'')$ going from one side to the other per second through the opening. If the mass of a molecule be m, then if $N'm = \rho'$ and $N''m = \rho''$ one has for G, the mass of gas flowing through s in unit time, the quantity

$$G = nm = \frac{1}{4}\bar{c}s(\rho' - \rho'').$$

Remembering that $\bar{c} = \sqrt{\frac{8}{\pi\rho_1}}$, where ρ_1 is the specific gravity of the gas under a pressure $\frac{1 \text{ dyne}}{\text{cm}^2}$ (roughly 10^{-6} atmospheres), and assuming from the gas laws that $\rho' = p'\rho_1$ and $\rho'' = p''\rho_1$, where p' and p'' are the pressures in A and B, then

$$G = \frac{s}{\sqrt{2\pi}}\sqrt{\rho_1}(p' - p'').$$

Replacing G by $Q = \frac{G}{\rho_1}$, then

$$Q = \frac{s}{\sqrt{2\pi}}\frac{1}{\sqrt{\rho_1}}(p' - p'')$$

or

$$T = \frac{Q}{p' - p''} = \frac{s}{\sqrt{2\pi}}\frac{1}{\sqrt{\rho_1}}.$$

This law should be obeyed for all gases where the thickness of the wall is small compared to s.

This can be tested experimentally in a simple way. Consider a pressure low enough so that the Knudsen régime of molecular flow is reached down a tube. If a thin plate with an opening s, small compared to the radius of the tube, be placed at one end, the rate of flow out of this opening can be easily measured. This really amounts to replacing chamber A by a tube having molecular flow. For such a tube it was shown in Sec. 78 that the outflow $Q' = \frac{1}{\sqrt{\rho_1}} \frac{p' - p''}{W'}$, where W' was a term representing the resistance to flow. Here $W' = \frac{3\sqrt{\pi}}{8\sqrt{2}} \int_0^L \frac{O}{A^2}\,dl$, where L is the length of the tube, O is its circumference, and A is its area of cross-section.

In analogy with this equation the quantity Q flowing through the hole s in the plate is given by the expression

$$Q = \frac{s}{\sqrt{2\pi}} \frac{1}{\sqrt{\rho_1}} (p' - p'') = \frac{1}{\sqrt{\rho_1}} \frac{(p' - p'')}{W}.$$

Here $W = \frac{\sqrt{2\pi}}{s}$ and acts as a resistance. The tube of area A and the opening in the plate of area s constitute two resistances in series whose value is thus $W + W'$. The flow Q'' through the system is then

$$Q'' = Q + Q' = \frac{(p' - p'')}{W + W'}$$

or

$$G'' = \sqrt{\rho_1} \frac{p' - p''}{W + W'},$$

where

$$W = \frac{\sqrt{2\pi}}{s}, \text{ and } W' = \frac{3\sqrt{\pi}}{8\sqrt{2}} \int_0^L \frac{O}{A^2}\,dl.$$

Knudsen carried out extensive measurements to test this law both at low and at higher pressures. It follows from the value of G'' that $T'' = \frac{G''}{p' - p''}$, must vary as $\sqrt{\frac{1}{\rho_1}}$ (*i.e.*, inversely as the square root of the specific gravity of the gas), and as $\sqrt{T}$, the absolute temperature. These he finds to hold very well. For the effusion portion of the equation, by putting in the value of W' for the tube, he can measure T. The results of some measurements are given in the table on p. 265.

	T obs.	T cal. $\frac{s}{\sqrt{2\pi}}\frac{1}{\sqrt{\rho_1}}$	T obs. $\times \sqrt{\rho_1}$
Hole No. 1:			
H_2	0.225	0.230	0.225
O_2	0.0565	0.0576	0.226
CO_2	0.0465	0.0491	0.218
Hole No. 2:			
H_2	2.98	2.92	2.98
O_2	0.757	0.729	3.13

The differences of the observed and computed values for hole No. 1 for H_2 and O_2 is of the order of 2 per cent, which is less than the error of experimental measurement in determining s. For CO_2, the error of 3.5 per cent is of the same order as the divergence in the two measurements of the area. The errors on holes Nos. 1 and 2 have opposite sign and thus indicate that the errors lie mostly in the measurement of s. The agreement, therefore, establishes the correctness of the factor $\frac{1}{\sqrt{2\pi}}$ within 3 per cent. This is in reality a proof of the Maxwellian distribution of velocities, for, had all the molecules had the same speed, a constant error of 8.6 per cent would have been found for both measurements.

80. Heat Conduction at Low Pressures.—When the consideration of heat conduction at low pressures is begun, as was stated in Sec. 76, the importance of the transfer of heat from and to the surfaces becomes greatly enhanced. Let the discussion first be extended to the mechanism of heat transfer from gas to solid irrespective of the pressure. Assume a metal surface at one temperature and the gas at a uniform higher temperature. Heat then passes from the hot gas to the cooler metal by the following mechanism: If the gas has the same temperature T_1 throughout, molecules having a velocity appropriate to the temperature, on the average, start from a layer one mean free path away and strike the surface at a rate $\frac{N\bar{c}}{4}$ per cm² per second, where N is the number of molecules per cm³ and $\bar{c}$ the average velocity. Each of these carries an energy corresponding to its specific heat. If it be assumed that there is no specular

reflection and that all molecules striking the surface attain thermal equilibrium with it, these molecules leave the surface with the lower velocity corresponding to T_2 the temperature of the metal. From this consideration the rate of heat transfer from the gas to the solid can be computed. If it be assumed that this transfer takes place across the distance of a mean free path, a coefficient of heat conductivity from gas to solid can be estimated by taking the temperature gradient as $\frac{T_1 - T_2}{L}$. The value thus computed is, however, a hundred fold or even more than that computed from actual observed heat transfers. This has led some writers, especially in the engineering field, to postulate a heat-insulating layer, or a layer of lowered heat conductivity in the gas next the solid. Such a picture is distinctly misleading and even wrong. The fact that the molecules leave the surface at a temperature T_2 at once furnishes a clue to the question, for these molecules collide in their first free path with the molecules of the gas T_1. Since they must be nearly equal in number in the first free path, collisions here result in a redistribution of energy, so that the average temperature in this layer is not T_1 or T_2 but has an intermediate value. As the molecules leaving the surface make more and more impacts, they acquire more nearly the temperature of the gas T_1. Thus the temperature gradient does not exist right up to the last free path from the surface, but the gradient extends over many free paths, perhaps even as many as 100 free paths from the surface. It is the existence of this gradient which limits the rate of heat transfer to the surface. In attempting to increase the heat conductivity it is necessary to increase this gradient. This could only be accomplished by removing the cool molecules to the interior of the gas as soon as they leave the surface and supplying new hot ones to replace them. It seems possible that by setting the gas into a violent mass motion one could accomplish this (*i.e.*, by the use of hot blasts of gas). If, however, one considers that the blast velocities usually achieved are small compared to thermal velocities which would be required to remove the cooled molecules from the surface, the futility of this method is at once seen. Furthermore, the absence of slip at higher pressures makes this difficult, for the gas has a sharp velocity gradient near the surface. If it were possible to generate a *molecular* turbulence at or near the surface, the difficulty might be in part overcome. Thus far, no success

has been achieved in this direction. The "insulating layer" at the surface is therefore nothing but the slowly moving (stagnant) layer of gas near the surface in which a gradual temperature gradient is set up by heat interchanges of a kinetic nature among the gas molecules.

As the pressures are reduced, however, these conditions rapidly change, for as soon as the mean free path becomes very great the slip for moving gases manifests itself. But more important than the slip is the fact that in the exchange of heat through the gas from a heated surface to a cooler one the molecules leaving the cooler surface do not meet enough heated molecules to get into equilibrium with them, before they reach the hotter surface heating the gas. Thus, the problem of heat conduction at low pressures at once involves not only the conduction from gas to solid surface, but rather the transfer from one surface to the other by means of the gas molecules. Furthermore, since the molecules now cross from one surface to the other before reaching equilibrium, it is obvious that, instead of the gradual transition of temperature from one surface to the gas, appearing to exist at higher pressures, there is an abrupt change of temperature from surface to the gas, whose value can be measured. It is this marked temperature drop at the solid gas surface that is the feature of the low-pressure heat-conduction phenomenon.

The existence of this drop was first postulated by Kundt and Warburg[2] as a result of the considerations following from their work on the flow of gases through tubes at low pressures, for with molecules leaving the surface at the temperature of the surface and exchanging energy with the rest of the gas at the first impact, the first layer of gas one free path away must be warmer than the solid. At high pressures a free path is so small that it cannot be detected, but as the free paths become larger the gradient must come to light. Von Smoluchowski[13] investigated this experimentally and found it to exist. He found, however, that it was greater for H_2 than for air. This he interpreted as meaning that the H_2 molecules, because of their small mass, exchanged less momentum with the molecules of the surface, and thus retained more of their initial energy than the air molecules did. Thus, the gradient at the surface was steeper in H_2 than in air. Certain experiments of Knudsen[14] on the absolute manometer and other low-pressure phenomena led him to conclude that apparently the rebounding gas molecules from a solid surface did not reach

temperature equilibrium with the surface. In his case, H_2 also showed the strongest departure from the anticipated behavior. A somewhat similar conclusion was also arrived at by Soddy and Berry,[15] who investigated the heat conductivity of various gases at higher pressures and found that the lower the specific gravity of a gas the more their results departed from the theoretically expected value. Knudsen therefore decided that these departures from anticipated laws needed more extended investigation. Since, however, the theory of heat conductivity at higher pressures was not completely successfully solved theoretically, Knudsen[16] felt that an investigation of these deviations at lower pressures where simpler theoretical laws obtain, and the deviations are even greater, would prove of value. In a masterful experimental investigation accompanied by a theoretical investigation he sets forth the conclusions which he draws. The interpretation of his results are called into question by von Smoluchowski[17] in a later theoretical paper. As will be seen, the objections raised by von Smoluchowski deal only with certain details of Knudsen's work. In fact, he accepts the general point of view of Knudsen as more satisfactory for very low pressures than his own. The work of Knudsen will thus be given, followed by the discussion of Smoluchowski.

The theory of Knudsen proceeds as follows: He assumes two parallel plates A_1 and A_2 opposite each other, and that they have *absolutely rough* surfaces. That is, that they have surfaces that are so constructed that when molecules strike them they bound back and forth enough times in the pores of the surface that they acquire the temperature of the surface on leaving. This assumption is really something more than the assumption of the *random direction of emergence*, when the particles leave the surface, first made by Maxwell in explaining slip, for in a random direction of emergence but one or two impacts are needed with the surface, while to gain thermal equilibrium with the surface the molecule must make many more impacts. Call T_1' and T_2' the temperatures of the two surfaces, and $\bar{c}_1$ and $\bar{c}_2$ the average velocities of the molecules leaving A_1 and A_2. It is further essential to assume that the molecule of mass m and velocity c has an energy $\frac{1}{2}mc^2$ only. This means that if one has a molecule not an atom, one must, for simplicity, first regard only its translatory energy, and leave out the other forms of rotational or

vibrational energy, for it is obvious that these energies enter into the exchanges in a different fashion from the translational energy. The latter can be introduced into the discussion at a later point.

As the molecules leaving A_1 have one velocity c_1 while those leaving A_2 have another value c_2, the equilibrium conditions will have to be differently formulated. Assume dN_1 molecules of velocity components between c_1 and $c_1 + dc_1$ *directed away from* A_1. These will strike A_2. If there were dN molecules per cm³ having *all* directions relative to A_1, then $\frac{1}{4}dNc_1$ molecules would strike 1 cm² of A_2 per second. But $\frac{dN}{2} = dN_1$ by the definition of dN_1, therefore $\frac{1}{2}dN_1c_1$ molecules strike the cm² of A_2 per second. Similarly, $\frac{1}{2}dN_2c_2$ molecules of velocity between c_2 and $c_2 + dc_2$ having their components directed away from A_2 will strike a cm² of A_1 per second. Thus, if the molecules striking A_2 did not emerge again from A_2, the energy gain of A_2 would be $dE_1 = \frac{1}{2}dN_1c_1\left(\frac{1}{2}mc_1^2\right)$. Hence $E_1 = \frac{1}{4}m\int_{c_1=0}^{c_1=\infty} c_1^3dN_1$. From Maxwell's distribution law,

$$dN_1 = \frac{4N_1}{\alpha_1^3\pi^{1/2}}c_1^2e^{-\frac{c_1^2}{\alpha_1^2}}dc_1,$$

whence

$$E_1 = \frac{1}{4}m\frac{4N_1\alpha_1^3}{\sqrt{\pi}}.$$

This at once is converted to the form $E_1 = \frac{\pi}{8}mN_1\bar{c}_1^3$. In a similar manner $E_2 = \frac{\pi}{8}mN_2\bar{c}_2^3$. Now E_1 is received by A_2 per cm² per second and E_2 is given up to A_1 from A_2. As the areas are equal, the net gain E_T of translational energy by A_2 per cm² per second must be $E_1 - E_2$. Thus the gain of energy of A_2 is

$$E_T = \frac{\pi}{8}m(N_1\bar{c}_1^3 - N_2\bar{c}_2^3).$$

Now the molecules that strike A_2 per cm² per second, if there are N_1 molecules of average velocity $\bar{c}_1$ with velocity components

towards A_2 per cm^3, are $\frac{N_1\bar{c}_1}{2}$. In a similar fashion the number that strike A_1 is $\frac{N_2\bar{c}_2}{2}$. As the molecules leaving these surfaces must equal those arriving when equilibrium is established and no molecules escape from between the plates,

$$\frac{1}{2}N_1\bar{c}_1 = \frac{1}{2}N_2\bar{c}_2.$$

Again, if the two plates be surrounded by gas molecules at an average speed $\bar{c}$ and there are N of these per cm^3 in order that the pressure between the plates remain constant, the number of molecules passing out through the edges from between the plates must equal the number passing inward from outside. If E be the area at the edges the equilibrium is established when $\frac{1}{4}N_1\bar{c}_1E + \frac{1}{4}N_2\bar{c}_2E = \frac{1}{4}N\bar{c}E$, or $2N_1\bar{c}_1 = N\bar{c}$,

whence
$$N_1\bar{c}_1 = N_2\bar{c}_2 = \frac{N\bar{c}}{2}.$$

The expression for E_T then becomes

$$E_T = \frac{\pi}{16}Nm\bar{c}(\bar{c}_1^2 - \bar{c}_2^2).$$

Since
$$\bar{c} = \sqrt{\frac{8}{\pi}}\sqrt{\frac{T}{273}\frac{1}{\rho_o}}$$

where T is the absolute temperature and ρ_o is the specific gravity of the gas at 273° abs. and a pressure 1 $\frac{\text{dyne}}{\text{cm}^2}$, then

$$E_T = \sqrt{\frac{2}{\pi}}p\frac{1}{\sqrt{\rho_o}}\frac{T_1 - T_2}{\sqrt{273T}},$$

where the analogous expressions for $\bar{c}_1$ and $\bar{c}_2$ are introduced and p is the pressure in dynes per cm^2 in the space between the plates. Thus the energy transferred from A_1 to A_2 per cm^2 per second is in terms of the pressure of the gas and the temperatures T_1 and T_2 of A_1 and A_2, and the temperature T of the gas.

This was deduced on very simple assumptions. Among others, attention was focused only on the transfer of translatory energy. If now rotational energy also contributes to heating the plates, then it must be included. The ratio k of the translational e_1, and rotational e_2, energies to the translational energy alone is

$k = \dfrac{e_1 + e_2}{e_1}$. This, in turn, can be placed equal to $\dfrac{\frac{2}{3}c_v}{c_p - c_v}$, for from Sec. 92

$$\gamma = \frac{c_p}{c_v} = \frac{\dfrac{2}{3} + \dfrac{e_1 + e_2}{e_1}}{\dfrac{e_1 + e_2}{e_1}},$$

whence
$$(\gamma - 1)\frac{e_1 + e_2}{e_1} = \frac{2}{3}$$

and
$$k = \frac{e_1 + e_2}{e_1} = \frac{2/3}{(\gamma - 1)}.$$

Now so far in the theory $e_1 = \frac{1}{2}mc^2$, the translational energy alone has been used in the heat transferred to A_2. Actually, $e_1 + e_2$ is transferred by each molecule. This would mean that $k\left(\frac{1}{2}mc^2\right)$ gives the energy transferred by each molecule, provided it is assumed that *for each molecule* $e_2 = (k - 1)e_1$ as the equation demands. The correct value of E_T would then be multiplied by the factor $k = \dfrac{2/3}{(\gamma - 1)}$, where γ is the ratio of the specific heats.

This treatment does not satisfy Knudsen, for he states that, while, on the average, in impact between molecules the net relative values of rotational and translational energies may not be altered, the relative values in each molecule are changed after the encounter. He assumes that the two quantities are distributed independently among the molecules, but that, on the average, they bear a definite ratio to each other. This requires that the value of E_T be redetermined averaging the rotational energies separately under this assumption. A_2 receives $\frac{1}{2}dN_1c_1$ impacts per cm² per second. Each impacting molecule carries the energy $\frac{1}{2}m\bar{c}_1^2$, where $\bar{c}_1^2$ is the *average squared velocity*. Since $e_2 = (k - 1)e_1$ then the rotational energy carried is $\frac{1}{2}m\bar{c}_1^2(k - 1)$, and the energy transfer per cm² per second due to rotational or vibrational energies is

$$dE_1' = \frac{1}{4}m\bar{c}_1^2(k - 1)c_1dN_1$$

$$E_1' = \frac{1}{4}m\bar{c}_1^2(k - 1)\int_{c_1=0}^{c_1=\infty} c_1dN_1$$

$$= \frac{1}{4}m\bar{c}_1^2(k - 1)\bar{c}_1N_1.$$

Accordingly, this treatment differs from the translational case in that one computes $\bar{c}^2\int_{c_1=0}^{c_1=\infty} c_1dN_1$ here, while before one computed $\int_{c_1=0}^{c_1=\infty} c_1^3dN_1$. In this case the rotational velocities are averaged independently of translation. Likewise the rotational energy lost by A_2 is $E_2' = \frac{1}{4}m\bar{c}_2^2(k - 1)\bar{c}_2N_2$. Thus E_A, the total transfer due to rotational energy is, on reduction, as before,

$$E_A = \frac{3}{4}\sqrt{\frac{2}{\pi}}(k - 1)p\frac{1}{\sqrt{\rho_o}}\frac{T_1 - T_2}{\sqrt{273T}}.$$

The total energy carried is $E_T + E_A = E$, whence

$$E = \sqrt{\frac{2}{\pi}}\left\{1 + \frac{3}{4}(k - 1)\right\}p\frac{1}{\sqrt{\rho_o}}\frac{T_1 - T_2}{\sqrt{273T}}.$$

Putting in the value of k in terms of γ and putting for ρ the quantity $\frac{1409.2}{32} \times 10^{-12}M$, where M is the molecular weight, then

$$E = 1819.2\frac{\gamma + 1}{\gamma - 1}p\frac{T_1 - T_2}{\sqrt{MT}} \text{ in ergs.*}$$

Practically, E cannot be directly measured conveniently due to radiation and residual gases. By measuring E at two pressures for a given $T_1 - T_2$, Knudsen gets a quantity $\epsilon = \frac{\Delta E}{\Delta p\Delta T}$ which has the value

$$\epsilon = 1819.2\frac{\gamma + 1}{\gamma - 1}\frac{1}{\sqrt{MT}} \text{ in ergs.}$$

Thus for H_2, O_2, and CO_2 putting in the values of Lummer and Pringsheim for γ one has

* As will later be seen, while von Smoluchowski[17] agrees with the value for E_T, he gives reasons for believing that E_A is not correctly computed. It is in any case an approximation and a change in averaging will change E_A only a little numerically.

$$H_2 = 10.968 \times 10^{-6}\sqrt{\frac{273}{T}} \text{ gram-cal.}$$

$$O_2 = 2.803 \times 10^{-6}\sqrt{\frac{273}{T}} \text{ gram-cal.}$$

$$CO_2 = 3.045 \times 10^{-6}\sqrt{\frac{273}{T}} \text{ gram-cal.}$$

As earlier experiments by others had intimated, Knudsen found the values of ϵ in these gases less than the theoretical value. This he interprets as meaning that the molecules leaving A_1 are colder than T_1 and that those leaving A_2 are warmer than T_2, as they have not reached thermal equilibrium with the surfaces before being diffusely reflected. This might be classified by saying that the surfaces are not completely *molecularly rough,* and the term *molecular roughness* would then apply in the measure that the equations were fulfilled. In practice, therefore, the case for surfaces which are not molecularly rough must be considered. To take this into account, assume that $\bar{c}_1$ and $\bar{c}_2$ are the velocities of the molecules moving between the plates, $\bar{c}_1$ those going to A_2 and $\bar{c}_2$ those going to A_1. If the molecules had been in thermal equilibrium with the surface they had just left then they would have had the velocities $\bar{c}_1'$ and $\bar{c}_2'$. If one can write that $\bar{c}_1^2 - \bar{c}_2^2 = \beta(\bar{c}_1'^2 - \bar{c}_2'^2)$, the equation for translatory energy exchange E_T becomes

$$E_T' = \frac{\pi}{16}Nm\bar{c}\beta(\bar{c}_1'^2 - \bar{c}_2'^2).$$

Since $\bar{c}_1'^2 - \bar{c}_2'^2$ determines the temperature difference $T_1' - T_2'$ in the same manner as $\bar{c}_1^2 - \bar{c}_2^2$ determined $T_1 - T_2$, one can write simply $E_T' = \beta E_T$. Thus the coefficient of heat conductivity ϵ_1 between not completely roughened surfaces is related to the coefficient of conductivity between completely *molecularly rough* surfaces ϵ by the expression

$$\epsilon_1 = \beta\epsilon = \frac{\bar{c}_1^2 - \bar{c}_2^2}{\bar{c}_1'^2 - \bar{c}_2'^2}\epsilon.$$

Actually, it is necessary to investigate the changes at the surface in order to get a theoretical expression for β. The average velocity $\bar{c}_1$ is not uniquely determined by $\bar{c}_1'$, the temperature velocity for equilibrium, with T_1', the temperature at A_1. It also depends on $\bar{c}_2$, the temperature which the molecule had when it struck A_1. This relation could be expressed by

$$\bar{c}_1 = a\bar{c}_1' + b\bar{c}_2,$$

where a and b are constants. These must be so determined that when $\bar{c}_1' = \bar{c}_1$ and $\bar{c}_1 = \bar{c}_2$, the equations hold true, that is, $b = 1 - a$, for then $\bar{c}_1 = a\bar{c}_1' + (1 - a)\bar{c}_2 = (1 - a + a)\bar{c}_1$. Accordingly,

$$\bar{c}_1 = \bar{c}_2 + a(\bar{c}_1' - \bar{c}_2).$$

For plates large in dimensions compared to the distance between them, and whose surfaces are the same, a must be the same for both surfaces, and one can write

$$\bar{c}_2 = \bar{c}_1 + a(\bar{c}_2' - \bar{c}_1).$$

The addition of these two equations gives $\bar{c}_1 + \bar{c}_2 = \bar{c}_1' + \bar{c}_2'$, an equation which Knudsen has confirmed experimentally in earlier work. Subtraction of the two expressions gives $\bar{c}_1 - \bar{c}_2 = \frac{a}{2 - a}(\bar{c}_1' - \bar{c}_2')$. Multiplying the two expressions, then

$$\bar{c}_1^2 - \bar{c}_2^2 = \frac{a}{2 - a}(\bar{c}_1'^2 - \bar{c}_2'^2).$$

Thus β has the value $\beta = \frac{a}{2 - a}$. The fraction a of the velocity equivalent to the temperature of the surface which the molecule carries away with itself on leaving the surface is called the *coefficient of accommodation.* The heat conductivity between two large parallel similar surfaces is then given by

$$\epsilon_{11} = \frac{a}{2 - a}\epsilon = 43.46 \times 10^{-6}\left(\frac{a}{2 - a}\right)\frac{\gamma + 1}{\gamma - 1}\frac{1}{\sqrt{MT}} \text{ gram-cal.}$$

Thus if ϵ_{11} is measured, a can be determined.*

In practice, it is not easy to measure ϵ_{11}. There is, however, a very interesting case, and that is where one of the surfaces is a fine cylindrical wire and the other a concentric cylindrical surface about it. In this case the molecules strike the outer surface a great many times compared to the inner surface. The molecules leaving the inner surface A_2 will have a velocity $\bar{c}_2 = \bar{c}_1 + a(\bar{c}_2' - \bar{c}_1)$ as before. Those leaving A_1, the outer surface, will, due to the large number of encounters, have $\bar{c}_1 = \bar{c}_1'$. Thus $\bar{c}_2 - \bar{c}_1 = a(\bar{c}_2' - \bar{c}_1')$. In this case $\bar{c}_2 + \bar{c}_1$ does not equal $\bar{c}_2' + \bar{c}_1'$. Actually, for small differences in temperature the difference is not great, so that one can write $\bar{c}_2^2 - \bar{c}_1^2 = a(\bar{c}_2'^2 - \bar{c}_1'^2)$. A rigorous analysis of the error due to this assumption with

* This equation is of the same form as one independently derived by von Smoluchowski[17] from similar assumptions, and appears to be the correct form. The ϵ used by von Smoluchowski, however, does not contain the factor for E_A.

experimental verifications indicates that this holds quite well, and one can then assert that $\epsilon_{1\infty}$ for the concentric cylinders is given by $\epsilon_{1\infty} = a\epsilon$. Also one has that $\epsilon_{1\infty} = (2 - a)\epsilon_{11}$. Finally, Knudsen analyzes the case for two cylinders of dimensions which are of the same order of magnitude. The resulting equations are more complicated. He finds an expression ϵ_{rR} which gives the heat conductivity in terms of ϵ, a, and a function of a, r, and R, the radii of the cylinders. By using the same inner cylinder, varying the outer cylinder and measuring ϵ_{rR}, he is able to get two equations giving a and ϵ.

The considerations above were put to experimental test by Knudsen. The details of the experiments, because of their extreme ingenuity, merit a description. They are, however, beyond the scope of the text. A few of the results may be cited.

For H_2 in glass, a was found to be $a = 0.26$. This used in the expression for ϵ_{rR} gives $\epsilon = 11.1 \times 10^{-6}$. The value of ϵ from the kinetic-theory calculation outlined above is 11.0×10^{-6}. This agreement is *fortuitously good* and is better than the experimental uncertainties warrant. It is possible, from the observed value of ϵ, to deduce the heat conduction for three different types of surface conditions in H_2 from the relations of ϵ_{11} and $\epsilon_{1\infty}$.

Absolutely Rough Surfaces in H_2	Glass and an Absolutely Rough Surface	Two Glass Surfaces
$\epsilon = 10.97 \times 10^{-6}$ cal.	$\epsilon = 2.9 \times 10^{-6}$ cal.	$\epsilon = 1.67 \times 10^{-6}$ cal.

Thus it is seen how much the value of ϵ is cut down by smooth surfaces.

Knudsen also measured a in H_2, using a fine wire and a concentric cylinder, thus obtaining $\epsilon_{1\infty}$. The results showed a to vary with the temperature. It took on the values 0.35, 0.376, 0.423 at 0, −79.5 and −192°C. This may simply mean that at lower temperatures the energy exchange with the surface is more nearly complete. Experiments with platinum and platinum black surfaces in the three gases, H_2, O_2, and CO_2, gave the following table of values:

Pt	$a =$		
	H_2	O_2	CO_2
Polished	0.358	0.835	0.868
Slightly coated with black	0.556	0.927	0.945
Heavily coated with Pt black	0.712	0.956	0.975

In what follows, in his paper, Knudsen carries over the notion of the accommodation coefficient to the case of heat conduction at higher pressures. He arrives at an expression for K, the coefficient of heat conductivity, using his expression for ϵ in gases at low pressures by considering heat conduction in the gas at higher pressures taking place over a region of the order of magnitude of the mean free path. It involves the unknown factor $x_1 = kL$, which gives the average distance from which the molecules come that carry the heat through the layer considered. It really gives x_1 as the distance of the temperature drop in the gas. With these notions, an expression is developed analogous to the expression for K for gases of O. E. Meyer. It reads:

$$K = 0.802\eta\frac{1}{M}\frac{\gamma+1}{\gamma-1}k(\text{gram-cal.})$$

while Meyer gets

$$K_1 = \frac{8}{3}0.802\eta\frac{1}{M}\frac{1}{\gamma-1}k_1(\text{gram-cal.}).$$

From measured values of K for O_2, k comes out 1.9 and 1.7 on the two theories. Both these equations, however, are severely criticized by von Smoluchowski and it is questionable whether they merit further discussion.

In a later paper, M. von Smoluchowski[17] discusses the paper of Knudsen and makes certain criticisms which are of value. In 1890, von Smoluchowski[13] had experimentally tested the variation of K, the coefficient of heat conductivity, as a function of the pressure. He had found it to be independent of the pressure down to low values of the pressure. At the lower pressures he had observed departures from the predicted law. These he explained as being caused by the fact that the temperature drop at the surface of the wall was extending well into the conducting space at these pressures. The idea of this temperature drop, as has been said, came originally from the experiments of Kundt and Warburg on gaseous slip and was introduced by them. In two papers, von Smoluchowski[18] derived the theory of the temperature drop at surfaces, using two different viewpoints. In these deductions he also had to assume a lack of temperature equilibrium for molecules leaving the surface. His first theory assumed that molecules leaving a surface had a temperature Θ, while Θ_M was the average temperature of the molecules striking the surface and Θ_o was the temperature of the surface. This led to the relation $\Theta_M - \Theta = (1 - \beta)(\Theta_M - \Theta_o)$. This relation

is based on the same considerations as those used by Knudsen, and leads to Knudsen's expression if $(1 - \beta)$ be replaced by Knudsen's a. The second theory depended on the same type of reasoning used by Maxwell for the coefficient of slip, that is, he assumed that a fraction f of the molecules was "absorbed" and reemitted and a fraction $1 - f$ was reflected. Under these assumptions the molecules in the fraction f have the temperature of the wall and the $1 - f$ are uninfluenced by the impact. As was discussed under the theory of the coefficient of slip, Baule[7] shows that f is capable of a more detailed analysis and definition in terms of the number of impacts necessary to bring it to equilibrium with the surface and the chance that it had these impacts. This treatment is, however, rather more involved, and for simplicity's sake it is best to discuss the equations from the standpoint either of von Smoluchowski's first or second theory, though Baule's theory will be given in Sec. 84. The equations deduced gave formally analogous expressions for the heat conduction, but ones which led to different numerical results for gases at higher pressures. In the conduction at lower pressures the theories are simpler, and it turns out that for plane parallel plates von Smoluchowski's first mode of approach gives $\epsilon_{11} = \dfrac{a}{2 - a}\,\epsilon$, in agreement with Knudsen's theory, and that for the latter theory $\epsilon_{11} = \dfrac{f}{2 - f}\,\epsilon$. This has the same form as Knudsen's expression for a, but its meaning is different. There is an essential difference between the two cases from a theoretical point of view. In Knudsen's theory, the directions of the emitted molecules are all random and the Maxwell distribution law holds for emitted molecules no matter what the distribution of impacting molecules. In the second theory for the $1 - f$ molecules reflected these may be reflected in special directions if the impacting molecules have certain chosen directions. Von Smoluchowski points out, however, that both Warburg's experiments on the slip of H_2 and Knudsen's experiments on thermal transpiration (Sec. 82) show f for H_2 to be near 1, while the experiments of von Smoluchowski interpreted in terms of his second equation show that f must be much less. Thus von Smoluchowski's observed f is not the same as the f which comes from slip, and this indicates that for the thermal exchanges the accommodation coefficient a must be used, while for momentum transfer

another quantity f is used. In H_2, Knudsen found $a = 0.26$. It would seem, therefore, that the action of "surface roughness" is different for directional effects and temperature equilibrium on reflection, for it requires only one or two impacts of a molecule with the rough surface to wipe out all of its past history, while it takes many impacts for a molecule to reach thermal equilibrium with a surface.

In this connection von Smoluchowski points out that the calculation of E from E_T and E_A by Knudsen, in which the translational and rotational energies are treated as independent, is not justified. It is pointed out that it is likely that faster translational velocities will imply also faster rotations. Also it is pointed out that Knudsen's assumption that a is the same for rotation as for translation is somewhat doubtful. Both are valid criticisms. The first one, however, raises the question of independence of velocity components in Maxwell's distribution law as deduced in Sec. 33. It seems probable that, as the speed is altered after each impact, the correlation feared by von Smoluchowski is not an important one. To correct this, von Smoluchowski gives an expression with three unknown coefficients a_1, a_2, and β, to multiply ϵ by in order to get ϵ_{11}. The a_1 and a_2 are presumably the accommodation coefficients for translational and rotational energies, and β is a constant between 0 and $1/3$. On the other hand, in spite of von Smoluchowski's objections, the equation of Knudsen is a first step in the direction of a kinetic-theory formulation.

The problem of heat conduction at low pressures may be summarized with von Smoluchowski as follows:

1. A quantitative theory of heat conduction at very low pressures can, at present, be developed only for monatomic gases. From this the heat transfer per cm² per second between absolutely rough plane parallel surfaces is given by

$$\epsilon = \frac{4}{3}\frac{\rho CS}{\sqrt{6\pi}} = \sqrt{\frac{2}{\pi}}\frac{p}{\sqrt{273\,\rho_o T}},$$

where the first expression is von Smoluchowski's, putting the density as ρ, C the square root of the mean square speed, and s the specific heat at constant volume.

2. Knudsen's theory for polyatomic gases is doubtful, as is his theory of heat conduction at higher pressures.

3. Knudsen's experiments establish with great precision the proportionality of heat conduction at low pressures with the pressure.

4. To take account of the fact that the temperatures of molecules leaving a surface are not those of the surface, two theories are set forth. The first is *identical with Knudsen's theory of the accommodation coefficient and seems to be established by his experiments.*

5. The heat transfer for surfaces that are not molecularly rough is therefore given for plane parallel plates by $\frac{a}{2 - a}\,\epsilon$.

6. The fact that the accommodation coefficient is low in H_2 was known for some time from the work of von Smoluchowski, and Soddy and Berry. The work of Knudsen confirms this and shows how a varies with the nature of the gas and the roughness of the surface. It is doubtful to what extent the absolute values of a given by Knudsen are correct owing to the question of specific heats, but the relative values are correct.

81. The Absolute Manometer.[14]—The considerations thus far dealt with have shown that for very low pressures where the distance covered by the molecules is large compared to the distance between surfaces conditions arise that somewhat simplify the kinetic-theory treatment of the phenomena. In the preceding sections the flow of gases through tubes has been investigated as well as the transport of heat from one surface to another. The former phenomenon at the low pressures gave the volume of gas flowing through per unit pressure difference as independent of pressure. The heat conduction between parallel plates at the low pressures was, however, proportional to the pressure. It might be asked how the momentum transfer *normal* to the surfaces varies with the pressure of the gas. Investigation will show that it is proportional to the pressure. If this momentum transfer could be accurately measured in terms of mechanical force, it is possible that this would be a method of accurately measuring low pressures. This, in fact, Knudsen has achieved, and it is of interest to give here the theory of the absolute manometer of Knudsen.

To study momentum transfer, Knudsen makes use of the fact that the molecules leaving a heated surface have a higher velocity than those leaving a cool surface. Thus there will be a force between the two surfaces, and this can be measured by a sensitive balance.

Such forces have been in the past called radiometric forces, as they were in the past identified with the forces acting in the Crookes radiometer. In the latter instrument vanes blackened on one side, suspended in an evacuated chamber, were shown to have forces exerted on them when illuminated with radiant energy on the blackened side. Concerning the theory of such radiometers more will be said later. Here it may be mentioned that these phenomena are differentiated from the Knudsen case because they take place at much higher pressures, that is, well above 0.001-mm pressure. The effect at the higher pressures turns out to be, in reality, an edge effect, as long before postulated by Maxwell,[19] and not a surface effect, as is Knudsen's case.

Assume two plates A_1 and A_2 of different temperatures. It is also to be assumed that their area is large compared to the distance between them, which is, in turn, small compared to the mean free path of the molecules (*i.e.*, less than one-tenth the mean free path). It is assumed that A_1 has a higher temperature than A_2, and that hence the molecules leaving A_1 have a velocity $\bar{c}_1$ greater than $\bar{c}_2$ that of the molecules leaving A_2. Assume that there are N_1 molecules per cm³ of a velocity components directed towards A_2 from A_1, whose average value is $\bar{c}_1$ and whose average squared value is $\overline{G}_1{}^2$. Similarly, assume there are N_2 molecules per cm³ leaving A_2 with velocity components towards A_1 of average velocity $\bar{c}_2$ and of average squared velocity $\overline{G}_2{}^2$. It is then possible to get the number striking the surfaces per unit time and hence the momentum transfer per second, or the force per unit area. If one had considered the molecules which had velocity $\bar{c}_1$ components towards A_1 as well as away from it in an equilibrium case with A_2 absent, the number would have been $2N_1$ and the pressure would have been given by $\frac{2}{3}N_1m\overline{G}_1{}^2$. Now the pressure on A_2 is caused by only the molecules moving towards A_2, hence the pressure due to these molecules on A_2 is $\frac{1}{3}N_1m\overline{G}_1{}^2$, the molecules losing their energy on striking the surface. On the other hand, by similar reasoning, A_1 receives $\frac{1}{3}N_2m\overline{G}_2{}^2$ from the molecules leaving A_2 and striking A_1 with a velocity $\bar{c}_2$. The net momentum transfer to the two surfaces per cm² per second, and hence the force between them, will be the sum of these two, and thus K', the pressure per cm²

between the plates, is $K' = \frac{1}{3}m(N_1\overline{G}_1^2 + N_2\overline{G}_2^2)$. As was shown in the preceding section, the quantities $N_1\bar{c}_1$ and $N_2\bar{c}_2$ must be related by the expression $N_1\bar{c}_1 = N_2\bar{c}_2$ when equilibrium exists. Again, if the number of molecules outside the plates and their average velocity are designated by $N\bar{c}$ then, as was shown in Sec. 80, $N_1\bar{c}_1 = N_2\bar{c}_2 = \frac{1}{2}N\bar{c}$. Outside the plates the pressure is $p = \frac{1}{3}Nm\overline{G}^2$. The force outside per cm² is then the pressure outside, which is p, and the resulting force K acting on the plates per cm², that is, the force measured, is $K' - p$. This gives at once that

$$K = K' - p = p\left(\frac{K'}{p} - 1\right);$$

and substituting for p and K',

$$K = p\left[\frac{N_1\overline{G}_1^2 + N_2\overline{G}_2^2}{N\overline{G}^2} - 1\right].$$

Using the relation between $N_1\bar{c}_1$, $N_2\bar{c}_2$, and $N\bar{c}$,

$$K = p\left(\frac{\frac{1}{2}\left(\frac{\overline{G}_1^2}{\bar{c}_1} + \frac{\overline{G}_2^2}{\bar{c}_2}\right)}{\frac{\overline{G}^2}{\bar{c}}} - 1\right).$$

Now $\frac{\overline{G}}{\bar{c}} = \sqrt{\frac{3\pi}{8}}$ (see Sec. 35), and the question arises whether this relation also holds for $\frac{\overline{G}_1}{\bar{c}_1}$ and $\frac{\overline{G}_2}{\bar{c}_2}$. Where the difference of $\bar{c}_1$ and $\bar{c}_2$ is small this can be assumed to hold. Hence one may write $\frac{\overline{G}}{\bar{c}} = \frac{\overline{G}_1}{\bar{c}_1} = \frac{\overline{G}_2}{\bar{c}_2}$. The relation then takes the form

$$K = p\left(\frac{1}{2}\frac{\overline{G}_1 + \overline{G}_2}{\overline{G}} - 1\right) = p\left(\frac{1}{2}\frac{\bar{c}_1 + \bar{c}_2}{\bar{c}} - 1\right).$$

Whether $\overline{G}_1$ is equal to the temperature of the surface $\overline{G}_1'$ and whether $\overline{G}_2$ is equal to $\overline{G}_2'$ is certainly doubtful. In any case $\overline{G}_1' > \overline{G}_1 > \overline{G}_2 > \overline{G}_2'$ for such cases as the quantity $\overline{G}_1'$ is assumed greater than $\overline{G}_2'$. As was the case in Sec. 80, one can assume the existence of an *accommodation* coefficient a. Then, as in that section, one has the conditions

$$\overline{G}_1 = \overline{G}_2 + a(\overline{G}_1' - \overline{G}_2)$$

and

$$\overline{G}_2 = \overline{G}_1 + a(\overline{G}_2' - \overline{G}_1).$$

Thus, through addition, $\overline{G}_1 + \overline{G}_2 = \overline{G}_1' + \overline{G}_2'$. As it was assumed that the gas about both plates was in temperature equilibrium with A_2, then $\overline{G}_1 = \overline{G}_2'$. Making use of this and of the relation above, one gets K in the form

$$K = \frac{p}{2}\left(\frac{\overline{G}_1'}{\overline{G}_2'} - 1\right) = \frac{p}{2}\left(\frac{\bar{c}_1'}{\bar{c}_2'} - 1\right).$$

Again,

$$\frac{\overline{G}_1'}{\overline{G}_2'} = \frac{\bar{c}_1'}{\bar{c}_2'} = \sqrt{\frac{T_1}{T_2}},$$

where T_1 and T_2 are the absolute temperatures of the plates A_1 and A_2. Thus $K = \frac{p}{2}\left(\sqrt{\frac{T_1}{T_2}} - 1\right)$, or the pressure $p = \dfrac{2K}{\sqrt{\frac{T_1}{T_2}} - 1}$ in $\dfrac{\text{dynes}}{\text{cm}^2}$. For small temperature differences this changes to the simple form

$$K = \frac{p}{4}\frac{T_1 - T_2}{T_2} \text{ or } p = 4K\frac{T_2}{T_1 - T_2}\frac{\text{dynes}}{\text{cm}^2}.$$

Thus by knowing T_1 and T_2 and measuring K one obtains the pressure. Also it is seen that the momentum transfer per unit time K is proportional to the pressure.

The theory was tested experimentally by using a heated strip of platinum opposite and near one side of a platinum vane suspended at its center by a wire. The force constant of the torsion balance could be determined from its period of oscillation. The suspended vane had a mirror fastened to the suspension by which its deflection could be measured. The temperature of the suspended vane was that of the room. The other strip, representing A_1, was heated electrically and its temperature determined by its resistance, as it formed one arm of a Wheatstone bridge. An example of the results obtained in air for plates 0.55 mm apart is given below. First are given T_1 and T_2. T_2 was measured at the beginning of each experiment before heating T_1, on T_1. From the equation the pressure was calculated from the observed deflections. The pressure, as is seen, is quite constant. The average value 2.28 $\dfrac{\text{dynes}}{\text{cm}^2}$ is to be com-

pared with gage measurements which gave the air pressure as 0.20 $\frac{\text{dyne}}{\text{cm}^2}$ and the vapor pressure of the Hg at this temperature as 2.04 $\frac{\text{dynes}}{\text{cm}^2}$, the sum giving the observed pressure as 2.24 $\frac{\text{dynes}}{\text{cm}^2}$ in good agreement with the absolute manometer.

T_1	31.7	73.3	118.9	155.5	198.5	233.0
T_2	23.4	23.5	23.7	24.1	24.7	25.6
p	2.31	2.39	2.45	2.32	2.27	2.20
T_1	252.0	274.5	299.5	328.9	351.9	376.2
T_2	26.7	28.0	29.6	31.7	34.2	37.2
p	2.19	2.21	2.20	2.23	2.27	2.31

The experiments show that this gage does give good results when the conditions are fulfilled that L, the mean free path, is large compared to the distance between the plates. In the original article more precise forms of the apparatus are described and realms of applicability are discussed. For the scope of this text, however, the material given suffices.

In a later article, von Smoluchowski[20] discusses and revises Knudsen's theory of the absolute manometer. He points out that if this theory using the Maxwell factor f is applied one has Knudsen's expression for the force $K = \frac{p}{2}\left[\sqrt{\frac{T_1}{T_2}} - 1\right]$. If, however, the accommodation coefficient a is used, this equation is only an approximation. Complicated considerations, for which there is no room in this text, taking into account the fact that when a is less than unity it is necessary to deal with four velocities instead of two, lead to a new equation. This takes the form below, which, as is seen, includes the accommodation coefficient:

$$K = \frac{p}{2}\left[\sqrt{\frac{T_1}{T_2}} - 1 + \frac{1-a}{4(2-a)^2}\left\{\left(\frac{T_1}{T_2}\right) - 1\right\}^2\right].$$

When a is unity it goes over into the first expression.

82. Thermal Transpiration.[21]—If two vessels are filled with gas at atmospheric pressures and they are connected by a tube with a diameter large compared to the mean free path, it is usually assumed that if one tube is warmer than the other the pressures

will be the same in both vessels, although the densities vary inversely as the absolute temperatures, that is, in Fig. 46 on one side of the partition A one has a volume V_1, a temperature T_1, a pressure p_1, and a density ρ_1, while on the other side the temperature is T_2, the pressure p_2, the density ρ_2, and the volume V_2. Except for the small region of transition of temperature near A, it is asserted on the basis of observation that $\frac{p_1}{p_2} = 1$ and that $\frac{\rho_1}{\rho_2} = \frac{T_2}{T_1}$. This fact appears to be in conflict with the kinetic-theory assumptions. Suppose that the temperature difference T_1 to T_2 could be sharply confined to the plane at A. The kinetic theory would lead one to expect that, since $\bar{c}_1$ is the velocity equivalent to T_1, and $\bar{c}_2$ that equivalent to T_2, the equilibrium would demand $N_1\bar{c}_1 = N_2\bar{c}_2$. This means that $\frac{N_1\bar{c}_1}{N_2\bar{c}_2} = 1$. Multiplying both sides of the equation by $\frac{\bar{c}_1}{\bar{c}_2}$ one has at once that $\frac{N_1\bar{c}_1{}^2}{N_2\bar{c}_2{}^2} = \frac{\bar{c}_1}{\bar{c}_2}$ and thus that $\frac{p_1}{p_2} = \sqrt{\frac{T_1}{T_2}}$. But this is in contradiction to the first statement that $\frac{p_1}{p_2} = 1$. Obviously, both of these statements cannot be true at once. If the kinetic theory is to be correct, it must be shown that the two deductions are not incompatible. The discrepancy is cleared up when it is remembered that, in practice, one does not have an abrupt change in temperature at ordinary pressures. There always exists a transitional layer many mean free paths long in which the equilibrium mechanism may be very complex, and it is probable that the reactions of the walls enter in. Osborne Reynolds[22] was the first to see the consequences of these considerations and to grasp the rôle played by the walls. It was he who gave the name *thermal transpiration* to the phenomenon. If by some manner the temperature transition could be made quite abrupt, then the second law stated, that $N_1\bar{c}_1 = N_2\bar{c}_2$, must prevail and the conditions should be different. Such conditions would exist at low pressures where the temperature differences over a mean free path begin to be significant. Again, as in all such phenomena,

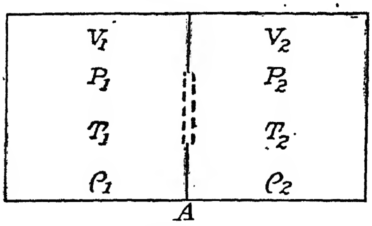

FIG. 46.

the walls play a large rôle, and assist in maintaining large gradients over a mean free path. The proof of the kinetic-theory assumption must lie in phenomena taking place when two bodies of gas are connected by a tube whose dimensions are small compared to the mean free path and in which there is a measurable temperature gradient. In fact, it is observed that under these conditions p_1 is not equal to p_2. A pressure difference is generated which depends on the pressure, molecular weight, coefficient of viscosity, and the diameter of the tube. The phenomenon can be made quite striking if a series of tubes with constrictions be arranged between two volumes and the constriction on the same side be heated to a high temperature. With 10 such tubes heated to 500°C. each, Knudsen achieved a pressure in one bulb 10 times that in the other. At ¼-mm pressure of Hg, and even at 3.5-mm pressure of Hg, he was able to get a pressure difference of 3 mm Hg in the two vessels. If the two vessels be connected by a second unheated tube this pressure difference will develop a flow of gas from one vessel to the other so long as the heating takes place. The direction of flow is from the region of lower to higher temperature. This must follow at once from the fact that such a flow builds up a pressure p_1 greater than p_2 in the ratio of $\sqrt{\frac{T_1}{T_2}}$ before the equilibrium is established. That the flow must go this way is seen at once also from the fact that N_1 is proportional to ρ_1 and hence to $\frac{1}{T_1}$, while N_2 is proportional to $\frac{1}{T_2}$. If T_1 is greater than T_2, then N_2 is greater than N_1 in the ratio $\frac{T_1}{T_2}$. The velocities $\bar{c}_1$ and $\bar{c}_2$ are, however, in the ratio $\sqrt{\frac{T_1}{T_2}}$, thus the product $N_1\bar{c}_1$ is less than $N_2\bar{c}_2$ by the ratio $\sqrt{\frac{T_2}{T_1}}$. Hence the flow will take place from cold to hot until the pressure ratio $\frac{p_1}{p_2} = \sqrt{\frac{T_1}{T_2}}$ builds up to check it. In case this does not occur, the flow will continue indefinitely as long as the gradient exists. If a body could be constructed with capillaries of the order of 10^{-5} cm, then temperature differences existing at atmospheric pressures should succeed in causing a transfer. Such capillaries actually do exist in porous clay vessels.

If one of these be provided with a heating arrangement to warm the gas inside and then be sealed off so that its only outlet emerges through water, cold air from outside will pour in and will bubble out through the water. The pressures observed with strong heating may amount to several centimeters of Hg, and some 100 cm^3 of gas per minute can be made to pass through a bulk of 100-cm^3 volume.

Thus the phenomenon of thermal transpiration is not an insignificant one and, further, it results in completely removing the apparent paradox facing the kinetic theory by an analysis of what occurs in the region of the gradient. It is therefore worth while to study it briefly before closing the subject of low-pressure phenomena. To begin the analysis, the phenomenon may be regarded as follows: If a plate were placed in the tube, a pressure difference due to the difference between $N_1\bar{c}_1$ and $N_2\bar{c}_2$ would be set up. If the plate were free to move, it would encounter a force against the walls of the tube. From the kinetic theory it is seen that, even were the plate absent, the walls would receive a tangential force when the temperature gradient exists. To study this assume a tube with a mild temperature gradient down it such that the density does not change appreciably over points a few free paths apart. Then the molecules striking it from one direction (*i.e.*, the warmer side) give it an impulse proportional to $n\bar{c}_1$ and those from the other direction give it an impulse $n\bar{c}_2$. If the temperature gradient is small, the number of impacts dn which unit surface receives from the solid angle $d\omega$ at an angle α is $dn = \frac{d\omega}{4\pi}N\bar{c}\cos\alpha$. Let it be assumed that $\frac{d\bar{c}}{dl}$ decreases in the direction of the tube, where dl is an element of length of the tube of the order of magnitude of the free path λ. Here also $\bar{c}$ is the average velocity of the molecules in the cross-section at the element, assuming $\bar{c}$ constant over the area of the cross-section. Assume a rectangular coordinate system with origin at the surface. The l-axis is along the tube, and the z-axis is normal to the surface. The axis λ of the solid angle makes an angle α with z and an angle β with l, where λ is the mean free path. The average velocity of the molecules will be the velocity corresponding to λ, and this velocity is $\bar{c} + \frac{d\bar{c}}{dl}\lambda\cos\beta$ when α is to the right of the yz plane and $\bar{c} - \frac{d\bar{c}}{dl}\lambda\cos\beta$ when it is to the

left of this plane, if $\frac{d\bar{c}}{dl}$ is assumed negative. In this case λ is small compared to the diameter of the tube. The momentum received per cm^2 of surface for impacts to the right of the cross-section in the yz plane for the solid angle $d\omega$ is

$$mdn\left(\bar{c} + \frac{d\bar{c}}{dl}\lambda\cos\beta\right)\cos\beta.$$

From the opposite side of the plane the momentum received from a similar solid angle is

$$mdn\left(\bar{c} - \frac{d\bar{c}}{dl}\lambda\cos\beta\right)\cos\beta.$$

The net momentum received per second per cm^2 from the gas as a whole for $d\omega$ is, therefore,

$$dM' = 2m\,dn\frac{d\bar{c}}{dl}\lambda\cos^2\beta,$$

whence

$$M' = 2m\int\frac{d\bar{c}}{dl}\lambda\cos^2\beta dn,$$

if it be assumed that the molecules leaving the surface are reflected equally in all directions. Putting the value of dn into M' and integrating, for M', the expression is obtained:

$$M' = -\frac{1}{16}Nm\bar{c}\lambda\frac{d\bar{c}}{dl}.$$

Introducing Maxwell's distribution of velocity then

$$M = \frac{3\pi}{128}Nm\bar{c}\lambda\frac{d\bar{c}}{dl}.$$

As $Nm\bar{c}\lambda = \frac{\eta}{0.30967}$ (see sec. 59), where η is the coefficient of viscosity, this becomes

$$M = \frac{-3\pi\eta}{128(0.30967)}\frac{d\bar{c}}{dl}.$$

The value of η here used is that of O. E. Meyer.
This is the tangential force exerted by the gas on unit surface of the tube. If this force just balances the force of the molecules, equilibrium results, and there is no streaming motion. Thus if there is no streaming in the tube

$$2\pi RM - \pi R^2\frac{dp}{dl} = 0,$$

where R is the radius of the tube. Whence the pressure gradient existing can be found at once as

$$\frac{dp}{dl} = \frac{3\pi\eta}{64(0.30967)R}\frac{d\bar{c}}{dl}.$$

Now $$\bar{c} = \sqrt{\frac{8}{\pi}}\sqrt{\frac{T}{273\rho_o}},$$

where T is the absolute temperature and ρ_o is the specific gravity of the gas at 0° for a pressure of 1 $\frac{\text{dyne}}{\text{cm}^2}$. As η varies with the temperature, according to Sutherland's formula one has

$$\frac{1 + \frac{C}{273}}{1 + \frac{C}{T}}\sqrt{\frac{T}{273}}$$

(see Sec. 62).

In H_2 gas, $C = 83$, $\eta_o = 84 \times 10^{-7}$, and $\rho_o = 88.62 \times 10^{-12}$. Also

$$\frac{1 + \frac{C}{273}}{1 + \frac{C}{T}}$$

can be set at 1.12 for two temperatures $T_1 = 800°$ and $T_2 = 300°$, whence solving, one has $R\frac{dp}{dl} = 0.0139$. For $R = 0.0187$, for the temperature difference 500°, $p_1 - p_2 = 371.9 \frac{\text{dynes}}{\text{cm}^2}$. With 10 such tubes in series separated by large-diameter tubes, $p_1 - p_2 = 3581 \frac{\text{dynes}}{\text{cm}^2}$. The observed pressure difference in an actual experiment gave $p_1 - p_2 = 3693 \frac{\text{dynes}}{\text{cm}^2}$.

As M is independent of pressure, this calculated pressure difference should be independent of the absolute values of p_1 and p_2. Experimentally, the observed pressure difference rapidly diminishes with increasing p.

To explain this case, the hypothesis of equal numbers of impacts from both sides, used in arriving at an expression for M, must be given up. This change would be expressed by assuming that at higher pressures streaming actually occurs in the tube and that this streaming is of such a nature that the wall receives less momentum than through M, for it is obvious that if N_1 and N_2 were different streaming would occur. Since this streaming goes from cold to hot, momentum due to the streaming gas would also reach the walls and this would be, in a sense, opposite to the

momentum received due to $\bar{c}_1$ being greater than $\bar{c}_2$ going from hot to cold. Also this streaming motion must progress in the direction of increasing temperatures, for it is in this direction that the walls act on the nearest gas layers with their tangential forces. As in equilibrium the gas mass as a whole must be at rest, there must therefore be a streaming on the inside of the tube in a sense opposite to the streaming along the tube, when this streaming along the tube occurs, for the streaming along the wall would build up a pressure difference, the pressure building up on the hotter side. The return of this moved gas mass which results from the walls, in view of the pressure difference built up, will naturally take place in the interior sections of the tube where the only resistance to overcome is the viscous action of the gas (see Fig. 47). It is seen that if such an action takes place the

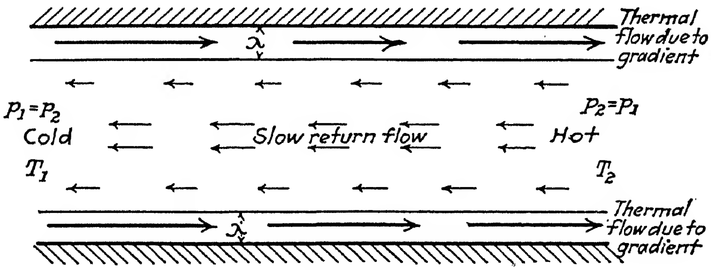

Fig. 47.

pressures in the two vessels will be equal, while, owing to the difference between $N_1\bar{c}_1$ and $N_2\bar{c}_2$, a streaming does take place. This, of course, will occur only at higher pressures. At the lower pressures, where the free paths begin to compare with the tube size, the simple equations deduced above hold, and a pressure difference will be maintained.

The flow under these conditions may now be investigated quantitatively. It is first necessary to calculate M, the momentum transfer, which every cm² of the wall receives per second through the temperature drop, because the molecules coming from one side have a higher velocity than those from the other side. In the present case, $\bar{c}$ is not the same for all molecules coming from any point in the cross-section of the tube. The isothermal surfaces will now make an angle with the walls. The velocity of the gas layers must decrease in the direction of the temperature gradient from the axis of the walls. Hence

the isothermal surfaces will make an acute angle with the walls in the direction of the temperature gradient. This will make the number of molecules which come from the left with particularly high velocities greater than those which come from the right with particularly low velocities. Thus the *old* expression for M is numerically less than the real momentum M received by the unit surface, regardless of the momentum which comes from the streaming gas along the surface. The new M may therefore be set as

$$M = -k_1 \frac{3\pi\eta}{128(0.30967)} \frac{d\bar{c}}{dl},$$

where k_1 is not a constant. It is unity for normal isothermal surfaces and must vary with the distortion of the isothermal surfaces from the simple cases where they are normal to the tubes. As the mean free path decreases, the angle with the normal increases, probably converging to a value less than 90°. That this is probable follows from the fact that the mass of gas flowing along the wall must equal the return mass of gas flowing in the opposite sense. Now the layer of gas flowing along the wall is confined in thickness to dimensions comparable with a free path. Thus the velocity of the returning gas mass in the center of the tube must be very small. The difference between these velocities must, therefore, approach a constant value, according to Knudsen, as the fraction $\frac{2R}{\lambda}$ increases towards infinity. Hence k_1 probably converges to a value somewhat greater than unity. It is seen, then, that for this case the momentum transfer is the *old* M multiplied by k_1. Besides this, owing to the velocity of the layer next the wall, the momentum B due to this must be given the wall. From Knudsen's work on the flow of gases through tubes (see Sec. 78) the following equations may be written: If B' is the momentum received by each cm² of surface per second for a mass of gas G moving down a cylindrical tube under a pressure gradient $\frac{dp}{dl}$, where B' is given by

$$B' = \frac{3\pi}{32} N\bar{c}mv\left(1 + \frac{2R}{\lambda}\right),$$

the mass of gas moves with an average velocity of slip V given by

$$V = v\left(1 + \frac{2RK}{\lambda}\right).$$

This value of V is the slip velocity, and therefore does not contain the factor depending on the increase of v towards the axis of the tube which exists in all cases of viscous flow at higher pressures. If this be included, the mass of gas G flowing through the tube per second is expressed by

$$G = -\left(ap + b\frac{1+\frac{2R}{\lambda}K}{1+\frac{2R}{\lambda}}\right)\frac{dp}{dl} \text{ (Sec. 78).}$$

In this, $ap\frac{dp}{dl}$ expresses the ordinary viscous flow and the second term the slip. Here, as in Sec. 78, $a = \frac{\pi}{8}\frac{\rho_1}{\eta}R^4$, and $b = \frac{4}{3}\sqrt{2\pi}\sqrt{\rho_1}R^3$, where R is the radius of the tube. Experiment showed (see Sec. 78) that the expression $\dfrac{1+\frac{2R}{\lambda}K}{1+\frac{2R}{\lambda}}$ was best represented by $\dfrac{1+0.81\frac{5R}{\lambda}}{1+\frac{5R}{\lambda}}$. At high pressures for which this deduction is being made, $\frac{5R}{\lambda}$ approaches infinity, and the above expression goes over to 0.81. Now B' may be written as

$$B' = \frac{3\pi}{32}N\bar{c}mV\frac{\left(1+\frac{2R}{\lambda}\right)}{1+\frac{2RK}{\lambda}}$$

by replacing v by the value of v in terms of V the slip velocity. Hence B' becomes

$$B' = \frac{3\pi}{32}N\bar{c}mV\frac{1}{0.81}.$$

For very small values of $\frac{2R}{\lambda}$, B' changes to

$$B'' = \frac{3\pi}{32}Nm\bar{c}V$$

(Sec. 78). Thus B' is somewhat greater than B''. This may come from the fact that, owing to the increase in velocity towards the axis at higher pressures, the momentum given the wall is in

this case greater when integrated over all space. Where the velocity of the gas decreases toward the axis, which is the case in question with the flow along the wall and return flow in the axis, the momentum B given the wall will be lessened. Assuming that the same factor 0.81 is active here, one can write that B, the momentum transfer to the wall by the layer moving near it, is 0.81 B''. Thus it may be roughly assumed that

$$B = \frac{3\pi}{32} Nm\bar{c}0.81V.$$

Now as $G = (ap + 0.81b)\frac{dp}{dl}$, and as the second term, $0.81b\frac{dp}{dl}$, gives the mass flowing through the tube per second due to the velocity of slip V, then one may equate the mass flow down the tube $\pi R^2\rho V = 0.81b\frac{dp}{dl}$, V being the relative velocity of the fast layer and the slowly moving central layer. Again, equilibrium in the tube demands that G is 0, hence $ap\,\frac{dp}{dl} = -0.81b\frac{dp}{dl}$, and thus $\pi R^2\rho V = ap\,\frac{dp}{dl}$, where ρ is the density of the gas. This gives a value of V which can be placed in B. B, accordingly, becomes

$$B = \frac{3(0.81)}{32}\bar{c}\frac{ap}{R^2}\frac{dp}{dl}.$$

The momentum given the wall in this case is, therefore, the modified M plus B. This momentum, as before, must equal the force exerted by the pressure difference set up, and one has finally

$$2\pi R(M + B) + \pi R^2\frac{dp}{dl} = 0.$$

If the values of M and B are placed in this equation, it becomes

$$\frac{dp}{dT} = \frac{0.00139\,\dfrac{1 + \dfrac{C}{273}}{1 + \dfrac{C}{T}}\,\dfrac{\eta_o}{\sqrt{\rho_o}}\,k_1}{R + 25.98\,\dfrac{\sqrt{\rho_o}}{\eta_o}\,\dfrac{1 + \dfrac{C}{T}}{1 + \dfrac{C}{273}}\,R^2\,\dfrac{p}{T}}.$$

Here C is the Sutherland constant for the change of viscosity with temperature.

For a tube of radius $R = 0.0187$ and for H_2, where $\frac{\eta_o}{\sqrt{\rho_o}} = 8.933$, at a temperature difference of 500°C., for which the Sutherland factor takes the value 1.12, one has

$$\frac{dp}{dT} = \frac{0.0139\ k_1}{0.0187 + 0.000910\frac{p}{T}}.$$

Integrated for a tube from T_1 to T_2, and putting $k_1 = 1$, the pressure difference in equilibrium becomes

$$p_2 = (p_1 - 0.718T_1)\left(\frac{p_1 + 21.28\ T_1}{p_2 + 21.28\ T_2}\right)^{0.034} + 0.718\ T_2.$$

The results of measurements made in H_2 with 10 tubes in series under the given conditions are included in the table below. The values are not computed for pressures less than 3.6 mm of Hg as the law as deduced does not hold in this region. At the lowest pressures the pressures should be given by the equation first deduced.

Pressures observed in mm Hg		Observed $p_1 - p_2$	Theoretical	
p_1	p_2		$p_1 - p_2$ for $k_1 = 1$	$p_1 - p_2$ for $k_1 = 1.45$
0.00978	0.00419	0.00559		
0.278	0.0314	0.247		
0.475	0.0476	0.427		
3.601	1.169	2.432	2.153	3.303
4.834	2.058	2.776	1.917	2.906
16.5	15.1	1.4	0.96	1.22
65.2	64.8	0.4	0.33	0.50
235.1	235.0	0.1	0.06	0.14
760.0	760.0	0.00		
For O_2				
3.133	1.747	1.386	1.027	

So far, two cases have been treated, that for very low pressures, where pressure differences due to transpiration are observable and directly calculable, the other at higher pressures, where the pressure differences produced are smaller and complicated by the flow

along the wall and the return flow; that is, for $\frac{2R}{\lambda}$ quite small and $\frac{2R}{\lambda}$ very large the theory has been successfully worked out, although only roughly in the last case.

Where $\frac{2R}{\lambda}$ has values near unity, it is necessary that the assumption made above, that the molecules which strike the surface come from a region, on the average, a free path away, so that they have the velocity proper to that region, be modified, for at the lower pressures the last impact may have been with a wall at less than a gas-free path distance. To do this, one must estimate the distance λ' covered by the molecule after striking the surface of the tube or some other molecule until it strikes the surface element considered. Analysis shows that $\lambda' = \frac{1}{\frac{1}{\lambda} + \frac{1}{2R}}$. If λ is large compared to $2R$, then $\lambda' = 2R$. This must replace λ in the first expression for M, where this expression for M is also multiplied by a factor k which varies with $\frac{2R}{\lambda}$. Thus $M = \frac{3\pi}{128} kNm\bar{c}\lambda \frac{dc}{dl}$. Putting in this correction and performing the operations as before,

$$\frac{dp}{p} = \frac{3}{4} k \frac{1}{1 + \frac{2R}{\lambda}} \frac{d\bar{c}}{\bar{c}}.$$

If $2R$ is very small compared to λ, the equation becomes

$$\frac{dp}{p} = \frac{3}{4} k \frac{d\bar{c}}{\bar{c}}.$$

Since
$$\frac{dp}{p} = \frac{d\bar{c}}{\bar{c}}$$

as was seen in the beginning of this section, k in this case is $\frac{4}{3}$. Putting T for $\bar{c}$ in the equation, then $\frac{dp}{p} = \frac{1}{2}\frac{dT}{T}$, whence $\frac{p_1}{p_2} = \sqrt{\frac{T_1}{T_2}}$. This is the result arrived at from the very elementary reasoning at the beginning of this section.

Where $2R$ is large compared to λ, $\lambda' = \lambda$. For this case k becomes unity and one has the expression first deduced. With

intermediate values of $2R$ with respect to λ, k can be assumed about $\frac{4}{3}$. Accordingly, $\frac{dp}{p} = \frac{1}{1 + \frac{2R}{\lambda}} \frac{d\bar{c}}{\bar{c}}$, putting $\frac{d\bar{c}}{\bar{c}} = \frac{1}{2}\frac{dT}{T}$, and

$$\lambda = \frac{1.12\sqrt{\pi}}{(0.30967)273\sqrt{8}} \frac{\eta_o}{\sqrt{\rho_o}} \frac{T}{p} = f\frac{T}{p}.$$

Integration gives

$$\log \frac{p_1}{p_2} = \frac{1}{2} \log \frac{fT_1 + 2Rp}{fT_2 + 2Rp}.$$

Call p_1 the pressure at the warmed transition between two tubes of radii R and R_1, where R_1 is greater than R, and, assuming that the above equation holds for both tubes, one has for the pressure p_2' at the temperature T_2 the relation

$$\log \frac{p_1}{p_2'} = \frac{1}{2} \log \frac{fT_1 + 2R_1p}{fT_2 + 2R_1p}.$$

Subtracting the two equations one has

$$\log \frac{p_2'}{p_2} = \frac{1}{2} \log \left(\frac{fT_1 + 2Rp}{fT_2 + 2Rp} \cdot \frac{fT_2 + 2R_1p}{fT_1 + 2R_1p}\right).$$

This gives as an approximation

$$\frac{p_2' - p_2}{p_2} = \frac{p}{f}(R_1 - R)\frac{T_1 - T_2}{T_1T_2}.$$

It is seen that p_2' for the wider tube is the greater; also that $\frac{p_2' - p_2}{p_2}$ is proportional to $T_1 - T_2$, to $R_1 - R$, and to p. This law, of course, holds only for the lower pressures.

As has been seen from the experiments, the theory agrees quite satisfyingly with the observations. This indicates that, while it may be in error in certain assumptions, it is, in the main, correct and can be accepted as explaining the phenomenon.

83. Radiometric Forces in Gases.—It was remarked in Sec. 81, where the force between two plates at different temperatures in gases at very low pressures was derived, that this phenomenon might be classed with the various other radiometric phenomena. In the sense that the forces involved are due to molecular impacts depending on differences of temperature at reduced gas pressures, they might be identified as belonging to the same class of phenomena as those usually termed radiometric. From the mechanical point of view, however, the resulting mechanisms are radically different in the two cases. The radiometric effects

which have been mostly used for measurements of radiation intensity are most effective and prominent in a pressure régime much higher than the régime investigated by Knudsen. Their maximum efficiency lies at about 0.05 mm Hg, the exact location of the maximum depending, of course, fundamentally on the dimensions of the apparatus. Aside from the fact that the theoretical treatment depends largely on questions of design and has been only incompletely worked out, the pressure régime involved makes it scarcely more than deserving brief mention in this chapter.

The repulsion of a radiated body under radiation was first observed by Fresnel. W. Crookes studied it beginning in 1873, and devised many different forms of the device. Among these was the well-known vane radiometer, in which light vanes blackened on one side were mounted about an axis free to rotate in a partially evacuated space. These radiometers are frequently seen in opticians' windows and are called after their discoverer the Crookes radiometer. Crookes found that the radiometric force was a function of the gas pressure, depended on the absorption coefficient of the wing surface, and was proportional to the intensity of radiation. Schuster showed that this was not due to light pressure. He suspended the chamber as well as the vane and found that the vane was moved relative to the chamber. This indicates that it was a relative force between vane and walls, and not the light pressure, which acted. Had it been light pressure, both vane and chamber would have been displaced. Donle investigated the forces keeping the pressure constant. The information gained by him and others, notably Nichols and Rubens,[34] and Nichols and Hull, dealt chiefly with the radiation side of the phenomenon and Nichols[35] developed a very useful radiometer for the study of radiant energy based on this action.

Even as early as 1874 the effect was ascribed as being due to the unequal bombardment of molecules produced on the two sides by differences of temperature. That actions of this sort do occur was seen in Sec. 81, where Knudsen's absolute manometer was discussed. The pressures where such simple actions occur are, however, much lower than those obtaining in Crookes' experiments, and it was soon noticed that the explanation given was in contradiction to the kinetic theory at the higher pressures. Many attempts were made in those days to explain and derive

quantitative theories for the phenomenon which would fit experimental facts. These largely failed for two reasons: In the first place, the pressure measurements until 1909 were not reliable, for it is only since Knudsen's work that low-pressure measurement has reached any degree of precision. In the second place, very few of the experiments were ever correlated with the temperature measurements on the vanes. The importance of the latter will be seen in later discussion. As a result of the analyses of the phenomenon, two rival schools were set up. The first group contended that repulsion was due to a surface-area effect, and was proportional to the blackened surface. This was contended by G. J. Stoney[23] and by Fitzgerald.[24] On the other hand, Maxwell,[19,33] with his remarkably clear vision, contended that the large portion of the areas of the vanes were inactive and that it was only at the edges that one had any stress arising from inequality of temperature in the gas. O. E. Meyer concurred with Maxwell in this view. On Maxwell's theory, therefore, no forces other than edge effects could cause the pressure. Recently, Miss Edith Einstein again attempted to derive a theory for forces proportional to the whole surface, in which she carried on Maxwell's calculations, using higher-order terms. Of this, more will be said later.

In more recent years, interest has again revived in this field, largely through the experimental work of Gerlach and Westphal,[25] Westphal[26] and Gerlach[27] independently, and finally Westphal.[28] Westphal in 1919 deduced a theory of the effects which virtually stood until 1924. In 1924, two theoretical papers appeared.* One was due to Hettner and Czerny[29] and contained an experimental test of some of their conclusions. It dealt with the repulsion type of radiometers, such as used by Nichols in radiation measurements. The other paper was by A. Einstein,[30] and dealt in a semiquantitative fashion with the Crookes type of radiometer. The content of these papers gives today a clear picture of the nature of the usual radiometric phenomena, and they will form the basis of this section. Suffice

* Recently the work of Hettner[58] has been carried further in a paper "The Theory of Photophoresis," Zeits. f. Phys. 37, 179, 1926. This paper carries to a successful conclusion the previous work and explains the whole phenomenon quantitatively including the queer negative photophoresis, (apparent attraction of light for certain small particles) first observed and named by Ehrenhaft.

it to state that both indicate the predominance of the edge of the vanes in the two phenomena, thus establishing the correctness of the view set forth by Maxwell[19,33] in his paper. The work of Einstein has recently received partial experimental confirmation by Marsh.[31]

Just preceding the work of Hettner and Czerny, Miss Edith Einstein[32] worked out a theory of the radiometer for pressures where the free path was not greater than the dimensions of the plates. This theory gave the variations of radiometric forces with pressure which were observed experimentally. The theory, however, led to radiometric forces proportional to the square of the heat flow in the gas. This would mean that the intensity of the forces should be proportional to the square of the intensity of illumination, while the observed forces are proportional to the first power of the intensity. Furthermore, Czerny made measurements of the absolute magnitude of the radiometer forces which showed them to be 10^4 times greater than those calculated from Miss Einstein's theory. From this Hettner and Czerny concluded that, while the effect predicted by Miss Einstein probably existed, it constituted but a small fraction of the observed effect.

In seeking for an explanation, Hettner and Czerny reverted back to the theory of Maxwell discussed in Sec. 77, in which Maxwell concluded that, because of temperature gradients at the surfaces of solid bodies, tangential forces could be set up which would produce a streaming along the surface. Such surface gas currents Maxwell suspected might be the cause of the radiometric effects, and were the basis of his suspecting the edges as being the seat of action. The tangential forces assumed by Maxwell were, however, proportional to the second derivative of the temperature. They would, therefore, although playing a rôle, cause small effects compared to forces produced by the first derivative of the temperature. Maxwell[33] had also calculated forces depending on the first derivative, but had not applied them to the radiometer.

The forces last referred to are, however, nothing other than the familiar forces discussed in the preceding section, and which led to the phenomenon of thermal transpiration. For very low pressures, this phenomenon was worked out by Knudsen, who also discussed the case at higher pressures. His considerations were worked out, however, for special cases, and were not particularly adapted to the problem in hand. Furthermore, they

were more or less first-order approximations. Maxwell's considerations were much more general. At his time, the relations between molecular impacts and surfaces were not known. The present-day knowledge enabled Hettner and Czerny to carry the latter calculations through in a more rigorous fashion than had been done before. They, in general, use Maxwell's method, which is based on the development of the distribution of velocity functions as powers and products of the velocity components. As this method in the form used is beyond the scope of this text, the results of their calculations only will be given. Calculation shows that the velocity of the layer next the surface relative and parallel to it, u_2, is given by the equation

$$u_2 - \zeta \frac{du_2}{dz} = \frac{3}{4} \frac{\eta}{\rho T} \frac{\partial T}{\partial x}.$$

In this equation ζ is the coefficient of slip of the gas, $\zeta = \sqrt{\frac{\pi}{2}}\sqrt{\frac{M}{RT}}\frac{\eta}{\rho}$ (Sec. 77), ρ is the density, η the coefficient of viscosity, T the absolute temperature, and z is a length along the axis normal to the surface, while x is the length along the axis chosen parallel to the temperature gradient. If for η one put K, the coefficient of heat conductivity for a monatomic gas, where $\frac{K}{\eta} = \frac{15}{4}\frac{R}{M}$, the equation becomes

$$u_2 - \zeta \frac{du_2}{dz} = \frac{1}{5} \frac{K}{p} \frac{\partial T}{\partial x}.$$

This equation gives the u_2 the same sign as the $\frac{\partial T}{\partial x}$, which signifies that the velocity is directed in the same sense as $\frac{\partial T}{\partial x}$ is positive. That is to say, u_2 goes from cold to hotter points along the surface. If one neglect the slip term, $u_2 = \frac{3}{4}\frac{\eta}{\rho T}\frac{\partial T}{\partial x}$. This for $\frac{\partial T}{\partial x} = 1°$ for air at room temperature has the value $\frac{392}{p}$ $\frac{\text{cm}}{\text{sec.}}$. If the pressure p is 392 $\frac{\text{dynes}}{\text{cm}^2}$, (0.294 mm Hg), the velocity will be 1 $\frac{\text{cm}}{\text{sec.}}$. It is, therefore, obvious that currents with considerable velocities can be set up for even small temperature gradients.

To compare their result with Knudsen's it is essential to calculate the tangential force $-p_{12}$ exerted on the wall by the gas. Calculation gives

$$-p_{12} = \frac{\eta}{2}\frac{\partial u_2}{\partial z} - \frac{3}{4}\frac{\eta}{\sqrt{2\pi}}\sqrt{\frac{R}{MT}}\frac{\partial T}{\partial x} + \frac{\eta}{2\zeta}u_2.$$

From the expression for u_2 above $\frac{\partial u_2}{\partial z}$ can be eliminated and then

$$-p_{12} = -\frac{3}{2}\frac{\eta}{\sqrt{2\pi}}\sqrt{\frac{R}{MT}}\frac{\partial T}{\partial x} - \frac{\eta}{\zeta}u_2 = \eta\frac{\partial u_2}{\partial z}.$$

Knudsen calculated $-p_{12}$ in Sec. 82 as

$$-p_{12} = -\frac{3}{128\cdot 0.31}\frac{\pi\eta}{}\frac{\partial c}{\partial x} \text{ for a resting gas.}$$

This transforms into

$$-p_{12} = -0.19\eta\sqrt{\frac{R}{MT}}\frac{\partial T}{\partial x}$$

while Hettner and Czerny's equation yields

$$-p_{12} = 0.30\eta\sqrt{\frac{R}{MT}}\frac{\partial T}{\partial x}.$$

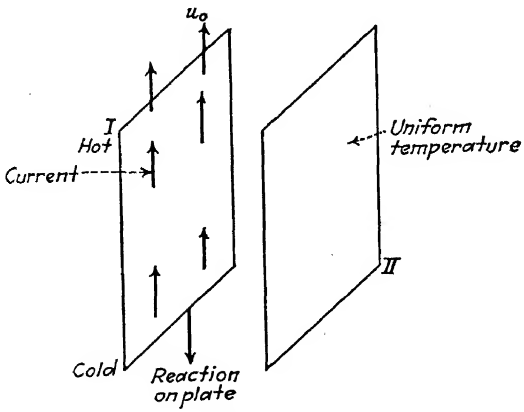

Fig. 48.

The difference lies only in the numerical factors 0.30 and 0.19. Knudsen's experiments gave twice the theoretical value for $-p_{12}$, and thus Hettner and Czerny's value is distinctly more satisfactory.

To carry this over to the case of a radiometer, consider the system shown in Fig. 48. Plate I is heated with a temperature

gradient such that the upper edge is warm while the lower edge is cold. Opposite it a cm away is plate II of uniform temperature throughout. There will be at the surface I a current from cold to hot of velocity u_o. The reaction to this will be a force on the vane downward. Call u_a the value of u_2 at the plate II, that is a cm distant from u_2. The velocity u_2 will then be given at any point x by

$$u_2 = u_0 + (u_a - u_0)\frac{x}{a}.$$

The hydrodynamic equations between the plates are fulfilled, together with the velocity conditions imposed by the equations deduced, when

$$u_0 - \zeta\frac{u_a - u_0}{a} = \frac{3}{4}\frac{\eta}{\rho T}\frac{\partial T}{\partial x},$$

and $u_a + \zeta\dfrac{u_a - u_0}{u_a} = 0$, whence it follows that

$$(u_a - u_0)\left(1 + \frac{2\zeta}{a}\right) = -\frac{3}{4}\frac{\eta}{\rho T}\frac{\partial T}{\partial x}.$$

Under the conditions where the equation applies, a must be large compared to a free path, while the coefficient of slip has the dimensions of a free path. Thus $\dfrac{2\zeta}{a}$ is negligible. The tangential force of reaction on the plane is then per cm²

$$-p_{12} = \eta\frac{\partial u_2}{\partial x_1} = \frac{\eta}{a}(u_a - u_0) = -\frac{3}{4}\frac{\eta^2}{a\rho T}\frac{\partial T}{\partial x}.$$

As one can measure p_{12}, and as a, ρ, T, η, and $\dfrac{\partial T}{\partial x}$ are known, the theory may be tested. This test is being carried out by Hettner and Czerny.[58]

It is now the question whether these tangential forces may not be able to explain quite a number of other of the radiometric effects. A qualitative discussion of a few of the more common types will be taken up at this point:

1. Rubens and Nichols designed a radiometer of the type shown diagrammatically in Fig. 49. Plate I is blackened and illuminated. Plate II is a conducting plate, or one that is uniform in temperature and not heated. It happens from the geometry of the system that the illuminated plate has a temperature gradient from the center C to the edges. The existence of such gradients has been proved experimentally by Marsh[31] on

blackened radiometer vanes of mica, by direct measurement. He observed, at 1.2-, 0.4-, and 0.04-mm pressure, temperature differences of 0.16, 0.24, and 0.28° on two points, 1 cm apart, of a vane of mica 0.45 mm thick when illuminated on the blackened side by light from a Point-O-Light lamp. The one point chosen was 1 mm from the edge, the other at the center of the vane. As a result of this gradient the gas will flow along the heated vane from the cooler edges to the center. As the opposite vane is cold and uniform in temperature, the return current of gas will flow from the center outward along the surface of plate II. Such a flow of gas as indicated by the arrows will, owing to gaseous viscosity, build up a pressure in the center. Thus one will have repulsion between the two plates. Hettner and Czerny calculated the radiometric force for this case, but do not give it. It is stated that the forces in this case for the same ratio of plate

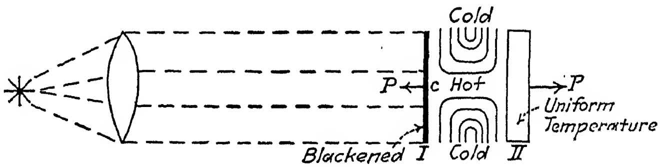

FIG. 49.

area to plate distance are greater than the one previously calculated for the lateral thrust on the vane.

2. If both surfaces I and II are illuminated, the currents then flow along both surfaces from the edges to the center. The return currents occur in the center. This arrangement therefore simply gives greater forces of repulsion compared to the hot and cold plate.

Perhaps one of the most striking proofs of this mechanism is in those forms of radiometers where the motion can take place in the direction of the sharp edges. As the edge is cooler than the central part, it will cause the metal to be given an impulse in the direction of the edge while the gas streams in the opposite sense. An amusing form of such a radiometer is one made of two half cylinders of bright tin, mounted on arms placed on a pivot. On illumination, these rotate about the pivot with the concave sides leading.

The actual calculation of the forces and their quantitative verification, however, must be confined to simple cases. In

most cases the complex nature of the interaction of the gas and the walls, the unknown temperature gradients, and the effects of the gas on cooling the vanes make accurate study nearly impossible. A word more in this connection might be said of the variation of these forces with pressure. From the theory the force K is proportional to $\frac{1}{\rho}$ and hence to $\frac{1}{p}$ for the higher pressures. On the other hand, at lower pressures in the Knudsen régime K is proportional to the number of molecules, that is, K is proportional to p. Thus, roughly, one may write $K = \frac{a}{p}$ for larger pressures and $K = bp$ for very low pressures. Whence one may write that $\frac{1}{K} = \frac{p}{a} + \frac{1}{bp}$ to a first approximation. This leads to Westphal's observed "symmetry" of the radiometer function in logarithmic presentation. For if one set $\sqrt{\frac{a}{b}} = p_0$, and $\log \frac{p}{p_0} = x$, then $K = \frac{\sqrt{ab}}{e^x + e^{-x}}$, which is symmetrical with regard to the maximum at $x = 0$, or at $p = p_0$. It must be borne in mind, however, that the pressure relations discussed hold only for constant temperatures and temperature differences. In most radiometric work these change radically with the pressure also and the importance of measuring the temperatures as well as the pressures must be emphasized when studying these effects.

In a paper published simultaneously with that of Hettner and Czerny, A. Einstein[30] treats in a qualitative but clear manner the theory of the action of the vane radiometer first made by Crookes. His considerations are as follows:

1. Take a body small compared with the mean free path placed in a gas space of large extent in which there exists a temperature gradient. The homogeneous temperature flux lies along the x-axis. All molecules are considered as having the same velocity u except for small differences representing the temperature gradient. It is further assumed that the molecules only move in the directions of the coordinate axes. The mean free path L is treated as a constant. This schematic representation of the gas will give results of the proper order of magnitude. Using more rigorous methods will cause only small changes in the value of a constant factor, as is the case with all refinements of kinetic-theory treatment.

Assume a surface element s whose size is small compared to L placed normal to the x-axis, and assume the absence of any mass motion of the gas. Then exactly equal number of molecules pass through s per second in opposite directions equal to $\frac{1}{2}(\frac{1}{3}Nsu)$, where N is the number of molecules per cm³. To account for the heat flow, the velocity of the molecules u_+ in the positive sense of the x-axis must be slightly greater than u and that of those on the negative side u_- slightly less than u. The heat flow sf through the surface is given by

$$sf = \frac{1}{6}Nsu\left(\frac{m}{2}u_+{}^2 - \frac{m}{2}u_-{}^2\right).$$

If one call $\frac{1}{2}mu^2 = \frac{3}{2}KT$, and if one assume that u_+ and u_- are appropriate to the temperatures existing at the place of their last collision (*i.e.*, at L cm away from s), then one has in place of the above expression

$$f = -\frac{N}{2}KLu\frac{dT}{dx},$$

for

$$\frac{1}{2}m\,(u_+{}^2 - u_-{}^2) = -\frac{3}{2}K\frac{dT}{dx}(2L).$$

In place of the surface area considered, let one now assume a small solid body of surface s. There will be more momentum given it per unit time from the positive side of the x-axis than from the negative side. Thus there will be an excess of momentum k in the direction of the positive x-axis. This is given by

$$k = \frac{1}{6}Nsu(mu_+ - mu_-).$$

If the impulse given due to the recoil of the impacting molecules is neglected, then k will also be the force on this surface. From this expression and the preceding one, the following equation results

$$k = \frac{sf}{u} = -\frac{1}{2}p\frac{L}{T}\frac{\partial T}{\partial x}s,$$

if it is assumed that u_+ and u_- are nearly equal to u, for

$$s = -\frac{1}{6}Nsu\frac{m}{2}(u_+ - u_-)(u_+ + u_-)$$

$$= k\frac{(u_+ + u_-)}{2}, \text{ or } fs = ku,$$

where p is the gas pressure. The quantity f is, of course, only the heat flow due to translational velocity. To get the velocity

v of the particle the frictional force K' of the gas on the particle must be calculated. This force arises from the fact that the particle gives every molecule it strikes the impulse mv. A simple calculation gives this as follows: Call v the velocity of the particle, and m its mass. The molecules striking it from behind gives $2m(u - v)$ of momentum to the particle, the one striking from in front gives $-2m(u + v)$. The number of collisions from behind in unit time is $\frac{1}{6}Ns(u - v)$ and from in front is $\frac{1}{6}Ns(u + v)$. The net momentum transfer in unit time is $\frac{1}{6}Ns \cdot 2m[(u - v)^2 - (u + v)^2]$

$$= \frac{1}{3}Nsm[-4uv].$$

The resisting force K' is, therefore,

$$K' = -\frac{4}{3}Nsu(mv).$$

Equating k and $-K'$,

$$v = \frac{1}{4}\frac{f}{RT\eta} = -\frac{1}{8}u\frac{L}{T}\frac{\partial T}{\partial x} = \frac{1}{4}\frac{f}{p}.$$

This velocity can be quite appreciable, and if the particle is small compared to L the velocity is independent of s as the equation shows. If L is 0.1 cm, $\dfrac{\partial T}{\partial x} = 30$, $T = 300°$, and in H_2 gas one obtains v of the order of 10^2 cm per second. At atmospheric pressure this would be 0.1 mm per second.

2. Consider next the effect of a small hole in a large thin partition placed normal to the heat flow. It is well known that in a vessel, even if its temperature is not uniform, there exists an equality of pressure. This holds as long as the dimensions considered are large compared to a free path as seen in Sec. 82. Thus if the small elements of the preceding paragraph had been replaced by a large plane normal to the temperature flow, even though a temperature difference existed on both sides, the pressures would be equal. Every molecule striking from the negative x direction has a velocity u_n on striking and leaves with a velocity u in the direction of the negative x. ν_n such impacts occur per second per unit area. The quantities u_p, u, and ν_p are the corresponding quantities on the positive side of x. It is assumed that u, the velocity of recession, is the same in the positive and negative senses of x. The condition for equality of pressure is that the total pressure $p = m\nu_n(u + u_n) = m\nu_p$-

$(u + u_p)$. Moreover, the heat flow must be the same on both sides of the plate, which is expressed by the equation

$$f = \frac{\nu_n m}{2}(u_n{}^2 - u^2) = \frac{\nu_p m}{2}(u^2 - u_p{}^2).$$

Dividing the second equation by the first,

$$\frac{2f}{p} = u_n - u = u - u_p.$$

If this be placed in the expression

$\frac{p}{m} = \nu_n(u + u_n) = \nu_p(u + u_p)$, and if $\frac{\nu_n + \nu_p}{2}$ be called ν and set equal to $\frac{Nu}{6}$, then $\frac{p}{m} = \nu_n\left(2u + \frac{2f}{p}\right)$ and $\frac{p}{m} = \nu_p\left(2u - \frac{2f}{p}\right)$. Whence

$$\nu_p - \nu_n = \frac{f}{up}(\nu_n + \nu_p) = \frac{Nf}{6p}.$$

If there were a minute hole of surface s in the plane, then $(\nu_p - \nu_n)s$ more molecules would pass through in the sense of decreasing x in unit time than in the other sense. Thus the hole would have a current of gas of velocity v given by $\nu_p - \nu_n = -Nv$ passing through it. From this equation and the preceding equation, therefore,

$$v = -\frac{1}{6}\frac{f}{p}.$$

Both these considerations belong really to the pressures in the Knudsen régime. They, however, furnish a clue to the problem of the radiometer at higher pressures, for consider a vane of area large compared to a free path but placed in a vessel whose dimensions were larger than that of the vane by many free paths. At some distance from the edge of the vane, equality of pressure will exist as deduced above. At some distance beyond the edge of the vane, if a temperature gradient exists, conditions will obtain in which a minute body would experience a force $\frac{sf}{u}$. At the edges of the vane a gradual transition will occur between the two conditions. The width of the zone where this occurs will have the dimensions of a free path L. There will thus be a pressure normal to the edge of the vane whose value per unit length of edge is given by

$$K = \frac{fL}{u} = -\frac{1}{2}p\frac{L^2}{T}\frac{\partial T}{\partial x}.$$

This will occur as long as the plate or vane is large compared to the free path.

For the case of a vane warmed on one side only, the equation is deduced in order of magnitude only and the deduction is not given. The force per unit length of the edge is found to be

$$K = -pL\frac{\Delta T}{T}.$$

It is seen that the equation predicts a force which will move the vane from the warm to the cold side. The force is not proportional to the area of the vane, but to the area of a strip along the edges one mean free path wide. Furthermore, in the radiometer heated on one side the force should be independent of pressure, for pL is a constant independent of pressure.

To test this out Marsh, Loeb, and Condon[37] made radiometers having vanes suspended from a quartz fiber. These vanes were so constructed that they had equal area moments about the suspension, but their edge moments were greater on one side than on the other. On illumination, such vanes *always deflected towards* the *side of greater edge moment.* The deflections were not in the ratio of the edge moments, however. Later investigation by Marsh[31] showed that this was due to the fact that the deflection is proportional to ΔT as well as to the edge moment. The side of the vane with the greater edge moment was, by measurement of its temperature, found to be markedly cooler than the side with the smaller edge moment. This was in keeping with the cooling effect of the edges mentioned by Hettner and Czerny. Again, the deflection should be independent of the pressure. A fourfold increase of the deflection was observed from 0.4 to 0.04 mm. It was found that the quantity ΔT also increased by a factor of 3 for the same pressure change. As the accuracy of temperature measurement was not high, it is impossible to say whether or not all the change in deflection with change in pressure could not be ascribed to changes in ΔT. Finally, the equation given by Einstein, which is good in order of magnitude only, was checked by actual measurements of the forces on the suspension, and the values of p, L, ΔT, and T observed. The force was found to be 0.02 dyne per cm of edge at a pressure of 0.03 mm The Einstein equation gave a force of 0.03 dyne per cm of edge at the same pressure and with the value of ΔT observed. This agreement is good considering the experimental uncertainties and the undetermined constant in the equation.

The field needs further careful experimental work under controlled conditions and with a knowledge of the temperatures involved. Work of this nature would help a great deal to guide further theoretical investigation.

84. Reflection of Molecules from Surfaces, Adsorbtion, and the Theory of Evaporation.—In the preceding sections of this chapter it has been seen how important the knowledge of the nature of the reactions of molecules with surfaces is for low-pressure phenomena. Some of the ideas have been developed as the various phenomena were discussed, and it was seen that a better understanding was gained as time progressed. It needed, however, more than this to clarify the situation and it was not until the study by Wood,[38] of what he called a "diffuse reflection" of atoms from the walls of a glass tube, that a more critical review led Langmuir[39,40,41] to publish a series of articles in which he connects this phenomenon with the adsorption on surfaces. Shortly after Wood's paper, Knudsen also published some results on this subject. The generalization by Langmuir, which because of its scope is very valuable, was independently derived by Frenkel,[43] who works out the equations in a more complete and noteworthy fashion. The content of the work of these two men will largely constitute this section.

Wood used jets of atoms of evaporating metal *in vacuo* similar to those studied by Dunnoyer.[44] He observed that such a jet of atoms on impinging on a cold surface was reflected back down the tube in a diffuse manner, showing no tendency to condense on the glass tube, although the temperature of the latter was way below the condensation temperature of the metal. If the glass in the case of mercury or cadmium was cooled with liquid air at the point of impact, condensation at once occurred. After it had started, even if the air was removed, the atoms continued to condense. If the glass target was not cooled but the bulb in the neighborhood was cooled, quantitative measurement of the deposit of metal on the walls showed that the atoms were diffusely reflected from the polished glass surface. That is, the amount of metal reflected at any angle with the surface followed the cosine law quite accurately. A clever geometrical modification of this experiment was carried out by Knudsen,[42] following Wood's first paper verifying the existence of the cosine law. At first Wood believed to have observed that there was an absence of deposit in a small zone where, according to the cosine law,

there should have been a slight deposition. Later experiments with cadmium did not show this. As will be seen further on, certain recent results of Chariton[45] and Semenow indicate that the reality of this zone has a bearing of considerable importance on the theories of the phenomena. The conclusion Wood drew was that there was a characteristic critical temperature above which atoms of a metal would not condense on a glass or non-metallic surface. This temperature, however, was far below the boiling point. On a metallic surface, at least one made up of their own kind of atoms, they will condense at once if the temperature is below the boiling point. For the cases where condensation did not occur, the direct measurement of the distribution of atoms leaving the surface indicated diffuse reflection. This observation by Wood of diffuse reflection of atoms was the first direct observation of the postulated diffuse reflection resulting from the experiments of Kundt and Warburg,[2] Knudsen,[11] and others. On the suspicion that possibly this was a case of condensation and reevaporation, Wood heated his target. He, however, still observed the cosine law.

In studying the evaporation processes of metals from filaments, as well as certain chemical effects caused by them, Langmuir had arrived independently at a somewhat different view of such phenomena. He believed that for the cases observed by Wood of what the latter termed diffuse reflection, one had no reflection in the real sense, but an actual case of condensation and reevaporation.

At first sight it might be thought that the distinction between a diffuse reflection and a condensation and reevaporation was rather a hair-splitting one, for in any case the condensed layer of atoms postulated by Langmuir cannot be appreciable in thickness. Thus the atoms must condense and reevaporate very rapidly. In fact, it is conceivable that the time of impacts with the surface, resulting in diffuse reflection, is quite the same as the time which the condensed atoms spend on the surface. If this were true, the two processes would *appear* to be indistinguishable in the limit, and perhaps they are so. This is only an appearance in the general case and the difference in point of view is an important one near the critical temperature which can be tested experimentally. If reflection takes place at a given temperature, and if there is a critical temperature of condensation, the condensation may occur sharply at the critical temperature and *will*

not depend on the density of the stream of impinging atoms. On the other hand, on Langmuir's condensation and reevaporation theory, condensation and evaporation will depend very markedly on the density of the atomic stream, for the rate of evaporation depends on the temperature, while the rate of condensation depends on the density of the atoms near the surface. For low stream densities where evaporation is rapid compared to condensation, the two phenomena may appear to be the same and in the limit may be so. Near the condensation temperature a considerable increase in the density of the stream of atoms could cause an accumulation of atoms on the surface which would disappear on reducing the stream density, provided a condensing layer did not fully form. No change would occur on reflection, for the number of reflected atoms would be equal to the number of the impinging ones. Long since Langmuir's article came out, Chariton and Semenow,[45] by a very ingenious scheme, have actually shown that the condensation on a surface with a temperature gradient down its length occurs at lower temperatures where the density of the atom stream is reduced. The evidence is not accurately quantitative and one may question it on other grounds.* Until it is more definitely proved, it must not be accepted as final. It, however, points strongly to the correctness of Langmuir's point of view.

That the point of view is justified in some cases follows also from considerations of the forces involved. It is obvious that the forces of the atoms of an element in the solid state are strong enough to cause condensation below the boiling point. When the atoms strike surfaces of other solids, there must also be adhesive forces of considerable magnitude active. That these should not be as great as the cohesive forces of the atoms in the solid is not surprising, although this does not seem to be the case for the monomolecular layers of gases condensed on metal surfaces. That the forces come into play is, however, shown by the condensation at lower temperatures. These forces must to some extent influence the interaction of the atoms and the surface. They must increase the duration of the time during which the atoms exist near the surfaces, and it is not impossible that in some cases they actually

* The doubt comes in on the question of the existence of a temperature gradient normal to the main temperature gradient which would make the edges of his plate cooler than the center. Chariton believes to have eliminated this but the question may well be raised.

cause condensation. Certainly, near the critical condensation temperature they do become of importance, and should cause just the effects observed by Chariton and Semenow. With this point of view it is important to analyze the results obtained in the other sections of this chapter and to see how they correlate with this viewpoint. Later it will be worth while to analyze the mechanics and the kinetic theory of the process further.

Langmuir opens his discussion with the evidence that atoms are not reflected from surfaces of their own atoms. The experiments of Wood on "reflection" and Knudsen on the rate of evaporation of mercury atoms from a mercury surface, as well as many experiments of Langmuir on rates of evaporation of filaments, indicate that practically no atoms of the metals studied are reflected from surfaces of their own atomic species. Weyssenhoff[46] studied the reflection of atoms of mercury from iron and gold surfaces and found a difference. This is probably in part due to the fact that the gold amalgamated with and dissolved the mercury. Thus not a gold surface, but one of mercury, is dealt with largely. The fact that gold amalgamates with mercury indicates strong adhesive forces and thus the suspicion of Langmuir about the rôle of surface forces may be supported. The experiment has otherwise no significance. In any case, no matter what the results observed between heterogeneous metals, the situation is clear for homogeneous substances, as Langmuir states. This argues strongly for the important rôle of the atomic forces in this case.

The next case considered is that of the heat conduction in gases. In this case there is the impact of gas molecules of a gas against the walls of a solid substance of another sort. There is little doubt but that these walls are partially covered with an adsorbed film of gas molecules which in part takes up the unbalanced surface forces of the substance. This layer depends for the extent to which it covers the surface on the gas pressure and the temperature, as Langmuir[40,47] has shown elsewhere.

The results obtained on heat conductivity at low pressures by Knudsen have been described in detail. They require interpretation in terms of a coefficient a, the "coefficient of accommodation" which gives the ratio of heat carried away by a molecule which leaves a surface (*i.e.*, is reflected from it) to the heat which it would carry away were thermal equilibrium established. The lowest value of a for a gas was that for H_2 in contact with a

polished glass or platinum surface where $a = 0.26$. For the heavier gases the value of $a = 0.87$ was found. For rougher surfaces higher values were found in all cases. Soddy and Berry[48] found a for H_2 in contact with Pt to vary from 0.25 at $-100°$C. to 0.15 at $+200°$C. For Ar, $a = 0.85$, while for He they found $a = 0.49$ at $-100°$C. and 0.37 at $+150°$C. At higher temperatures, Langmuir found $a = 0.19$ for H_2 and, for N_2, $a = 0.60$, the metal being W at 1500°K.

The rough independence of a of the chemical nature of the surface is to be expected from the reflection theory; although the theory of Baule, to be discussed later, makes the relative masses of surface molecules and impinging atoms a determining factor. The variations observed are great for the light molecules of H_2 and He atoms. The variation with the mass of the surface atoms largely gives changes that are so small that they fall within the accuracy of the results in magnitude. In order to explain the independence of the surface molecules, whose forces should vary widely among the metals, Langmuir is forced to assume that the similarity of surfaces is due to the adsorbed gas films on the metal surfaces. The effect of surface roughness indicates the existence of large cavities on the surface where multiple impacts are more probable, and hence thermal equilibrium can be more nearly reached. This is in line with Baule's theory. The decrease in a with temperature indicates a lessened effect of surface forces at higher temperatures, an effect well in line with Langmuir's theory. On the reflection idea, it would be difficult to explain, except on the basis of changes of the surface with temperature.

The experiments on viscosity at low pressures and the coefficient of slip have shown (as seen in Secs. 77 and 78) that under most conditions molecules are emitted from a surface on which they impinge with directions completely independent of the direction of motion of the impacting molecules. The only exceptions to this general rule, which also apparently holds for the metallic-reflection experiments of Wood and Knudsen, are some results of States[49] and Van Dyke,[9] using the rotating-cylinder method, of Gaede,[50] who used the flow of gases in tubes, and of Millikan,[51] who worked with oil drops. The results of States indicated that the molecules were reflected backward in their direction of incidence to a greater extent than the random reflection would warrant. He used, however, very rough surfaces. His measurements were made under conditions where the purity of his gases

could well be questioned due to evaporation of gases from the surfaces during the experiment. Blankenstein,[8] as stated in Sec. 77, repeated the experiments of States under more ideal conditions and found nearly completely diffuse reflection for a silver oxide film. He found the f of Maxwell's equation to be about 0.98 or more. The 2 per cent deviation could well be interpreted as a slight slip. The *"reverse specular reflection"* of States was not present. The results of Van Dyke, using the cylinder method, were of a different nature. He measured slip on the following surfaces: old shellac, clean brass, scratched brass, and watch oil. In his case he found values of f distinctly less than those observed by Blankenstein. The results are as follows: The slip for an old shellac surface was about 3 per cent higher for CO_2 and air than the value calculated on the assumption of perfectly diffuse reflection. This gives Maxwell's f as 0.985. In watch oil the values came out 21 and 12 per cent greater for air and CO_2 than the diffuse reflection would require. The Maxwell f in these two cases is 0.905 and 0.945. For the other two surfaces in air, intermediate results were obtained, while a result indicating "reverse specular reflection" was found for the scratched-brass surface in CO_2. The results on shellac and oil surfaces are in excellent agreement with the values computed by Millikan and his pupils from the motion of oil and shellac particles in a gas. The results of Millikan mentioned are the results of the measurements made on the slip for oil drops falling through a gas. A very critical theoretical analysis of this work of Millikan has recently been published by Epstein.[52] His analysis leads to the statement that the force encountered by a droplet of radius a, moving with a velocity V through a gas at a pressure when the dimensions of the drop are small compared to the mean free path, is given by

$$F = \delta \frac{4\pi}{3} N m \bar{c} a^2 V,$$

where N is the number of molecules per cm^3, m is their mass, and $\bar{c}$ their average velocity. In the equation, δ is a numerical coefficient which depends on the nature of the impacts of molecules with the surface. It takes the following values in the cases that are considered below:

1. For specular reflection, $\delta_1 = 1$.
2. For diffuse reflection with conservation of velocity, $\delta_2 = 13/9 = 1.444$.

3. For diffuse reflection with accommodation:
   a. For a complete thermal non-conductor one gets:

$$\delta_{3a} = 1 + \frac{9\pi}{64} = 1.442.$$

   b. For a perfect thermal conductor:

$$\delta_{3b} = 1 + \frac{\pi}{8} = 1.393.$$

Now Millikan's experimental results for such droplets give a force F_e represented by

$$F_e = \frac{6\pi(0.3502)Nm\bar{c}a^2V}{(A + B)}.$$

Thus $A + B = \dfrac{9 \times 0.3502}{2\delta} = \dfrac{1.575}{\delta}$, if Millikan's expression and that of Epstein are comparable.

Thus for the above cases $A + B$ should have the following values:

1. Specular reflection $(A + B)_1 = 1.575$.
2. Conservation of velocity:

$$(A + B)_2 = 1.091.$$

3. Accommodation:

$$(A + B)_{3a} = 1.093.$$
$$(A + B)_{3b} = 1.131.$$

In case a fraction s of the molecules suffer different laws of reflection

$$F = \sum s\delta \frac{4\pi}{3} Nm\bar{c}a^2V,$$

whence

$$A + B = \frac{1.575}{\sum s\delta}.$$

If one-tenth of the molecules are specularly reflected while nine-tenths are diffusely reflected the expression for $A + B$ becomes

$$A + B = \frac{1.575}{0.1 + 0.9\delta}.$$

This gives for (2), and for (3),

2. Conservation of velocity:

$$(A + B)_2 = 1.125.$$

3. Accommodation:

Insulating $\qquad (A + B)_{3a} = 1.127.$
Conducting $\qquad (A + B)_{3b} = 1.164.$

For oil drops, Millikan found 1.154. This agreement is satisfactory with $(A + B)_{3b}$ but does not deviate from the other values $(A + B)_{3a}$ and $(A + B)_2$ very much.

The decision between the views is, however, made definite through a consideration of the relation of the "internal conduction" through the sphere of the heat received from molecular impacts to the "external conduction." For the conditions of the experiment this leads to the conclusion that in Millikan's low-pressure measurements only the hypothesis of completely conducting spheres is justified. Thus it seems probable that from both oil-drop measurements and direct slip coefficient measurements at low pressures some surfaces at least show a definite small amount of specular reflection, that is, they have a Maxwell's $f = 9/10$.

As regards the experiments of Gaede, these show the presence of a "reverse specular reflection"—in some cases of considerable magnitude; that is, the amount of gas flowing through the tube is less than would be expected on diffuse reflection. This is in contradiction to the work of all other observers. It is likely that in his case, as in that of States, secondary factors entered in that do not affect the conclusions drawn here. Thus, in general, it may be concluded that diffuse reflection is the rule, *although in some special cases a small amount of specular reflection does occur.* Therefore, except in these cases, the general viewpoint of Langmuir is not contradicted.

Langmuir then studies the amount of reflection from surfaces by a study of the rate of chemical reactions. If one calculate from the rate of a surface catalysis the ratio of the number of molecules which react to the number of molecules striking the surface a fraction ϵ is obtained. He assumes that the molecules that react must stick. Thus $1 - \epsilon$ is the reflectivity, or at least the upper limit for it. The values of ϵ found in some reactions are interesting, but it would seem hardly convincing as regards reflectivity, for in a reaction of N_2 with CuO giving atomic nitrogen the value of $\epsilon = 0.002$ was found. This probably indicates that the reaction did not occur for every molecule which was not specularly reflected, for it is quite likely from slip measurements that f for N_2 on CuO is as high as 98 per cent or even more, and not 0.002. Again, it is possible that the value of ϵ in a reaction may be very much higher than the value of a, the accommodation coefficient. This is the case for H_2 molecules striking a filament of tungsten at 2700°K. Here ϵ was 0.68, while at 1500°K. the value of a for H_2

was 0.19. This Langmuir attributes to the fact that at 1500°K. the filament is covered with H_2 molecules, while at 2700°K. it is clean and bare and thus reacts with H_2 molecules. Finally, this, in general, raises the question whether a reaction in which the chemical forces acting between a specific surface and a specific gas permits generalization about the nature of impacts between surfaces where this is not the case. All that these results show is that chemical forces of one sort or another between surface and gas can influence the nature of the "reflection" process. Unquestionably, all degrees of intensity of forces exist. It is not surprising, then, that there should *be all possible degrees of condensation occurring on surfaces and possibly even cases where reflection in a true sense occurs, as it must do where specular reflection is observed.*

In a succeeding paragraph of Langmuir's paper the evidence is brought out that in the reactions of gas molecules there are some cases where every impact between two molecules capable of reaction results in an inelastic impact of combination. Leaving aside the particular question of the correctness of the interpretation of these results, they merely show that some molecules, when they collide under proper conditions, do not rebound elastically. This depends on the chemical forces involved and on the relative energies of the molecules. The existence of small molecular groups of molecules of water vapor in the saturated gas shown by many lines of evidence, such as the condensation experiments on ions,[53] and optical phenomena observed by Barus,[54] indicate that collisions under the proper circumstances may result in combinations. *Such a conclusion does not, however, in any sense imply that this is generally true.* In fact, all the evidence of kinetic theory indicates that this is a rare occurrence under conditions where the kinetic theory is generally applied.

As it seems definitely established that the heat-conduction experiments and slip experiments lead to two constants for the same surfaces whose values are different (*e.g.*, a and f), a consideration of the difference implied is worth while. This is well summed up in the theoretical treatment of Baule,[7] who assumes the solid to consist of a cubic space lattice of elastic spherical molecules or atoms which vibrate about their equilibrium positions with an average kinetic energy corresponding to the temperature. The gas molecules strike these and rebound from them following the laws of elastic impact. Call E_1 the mean energy of the incident molecules, E_2 the mean energy of the mole-

cules of the solid, and E' the mean energy of the gas molecules after one collision with the molecules of the solid. Then

$$E' = \beta E_1 + (1 - \beta)E_2.$$

In this equation β is given by the masses of the molecules and indicates the fraction of the energy of the incident molecules which they retain after one impact with the solid molecules. The value of β depends on the masses m_1 of the gas molecules and m_2 of the molecules of the solid, and is given by

$$\beta = \frac{m_1^2 + m_2^2}{(m_1 + m_2)^2}.$$

Now some of the molecules make more than one impact before escaping from the meshes of the surface. For simplicity, Baule assumes that all those leaving after more than one impact have the energy E_2. Assume a fraction ν (this ν must depend on the form of the surface) makes only one collision. Then if E is the energy of all molecules leaving the surface,

$$E = \nu E' + (1 - \nu)E_2$$

and thus

$$E = \beta\nu E_1 + (1 - \beta\nu)E_2.$$

Since the mean energy is proportional to their temperatures, it is possible to write

$$T = \beta\nu T_1 + (1 - \beta\nu)T_2,$$

or $(T - T_1) = (1 - \beta\nu)(T_2 - T_1)$, which gives a, the accommodation coefficient of Knudsen as

$$a = (1 - \beta\nu).$$

Baule also calculates the value of the accommodation coefficient for viscosity. This is a quantity related to Maxwell's f. Call v_1 the average velocity component parallel to the surface of the incident molecules, and v_2 the tangential velocity of the surface in the same direction. Also let v' be the average velocity parallel to the surface of the molecules which rebound after one collision. Calling γ the constant of velocity exchange for one impact, he finds from analysis that γ depends on the masses of the molecules of gas m_1 and surface m_2 and is given by

$$\gamma = \frac{m_1}{m_1 m_2}.$$

From this he deduces the relation

$$v' = \gamma v_1 + (1 - \gamma)v_2.$$

If, then, ν make only one impact and escape with the velocity v', while $1 - \nu$ are diffusely reflected, one has, if v be the average

velocity component of *all* the molecules leaving the surface parallel to it,

$$v = \nu v' + (1 - \nu)v_2.$$

This at once gives

$$v = \gamma\nu v_1 + (1 - \gamma\nu)v_2$$

or

$$(v - v_1) = (1 - \gamma\nu)(v_2 - v_1).$$

In terms of Maxwell's theory, f is the fraction of the molecules absorbed and $1 - f$ is the fraction specularly reflected. The quantity $(v - v_1)$ in terms of Maxwell's f is then given by

$$v = v_2 f + v_1(1 - f)$$
$$(v - v_1) = f(v_2 - v_1),$$

and thus Maxwell's $f = (1 - \gamma\nu)$ in Baule's terminology.

The measurements of f and a help to evaluate ν and to check the theory.

For H_2 in contact with *Pt*, $m_1 = 2$, $m_2 = 195$, hence $\beta = 0.98$, and $\gamma = 0.01$. If the value of $a = 0.26$ be taken from Knudsen's experiments, then $\nu = 0.76$ and this gives $f = (1 - \gamma\nu) = 0.992$. This should be the accommodation coefficient for viscosity. This agrees well with experiment where the values found lie between 98 and 100. For Ar in contact with Pt, $m_1 = 40$, $m_2 = 195$, $a = 1 - \beta\nu = 0.85$ (Soddy and Berry), $\beta = 0.72$, $\gamma = 0.17$, and $1 - \gamma\nu = 0.965$. Thus f for gases should decrease with increasing density of the gases, but is in any case near unity. Baule then analyzes the coefficient ν on various assumptions as to how the molecules on the surface are shadowed by others. Such assumptions must, perforce, be at best very hypothetical. Furthermore, Baule leaves out of account altogether the question of the action of surface forces. It is manifest that in many cases these are of prime importance, especially where the atoms condense on impact. It was the emphasis of this point of view which was Langmuir's great contribution. His analysis is given in the article in the *Physical Review*[39] just quoted. Since the article was written, and on the basis of the later work of Chariton and Semenow,[45] Frenkel[43] has developed the theory in a more precise manner, which will, therefore, be developed here.

Before the question is treated at all, the general problem of the mechanism of condensation and evaporation from a surface might be analyzed from the standpoint of the kinetic theory, for in this case one first meets the effect produced by surface

forces in kinetic theory. As the treatment of this subject is not easily found, it will be included at this point. The treatment is taken from Jellinek's[57] "Lehrbuch der Physikalischen Chemie," vol. 2, page 246.

Imagine a plane surface of liquid in *equilibrium* with its vapor. This demands that three conditions be fulfilled. The first is that from each side of the surface of the liquid as many molecules pass in one direction as in the other. That means that the rate of condensation equals the rate of evaporation. The second is that, as temperature equilibrium also exists, the kinetic energy carried through the surface in one direction equals that carried through in the other. The third condition is that as much momentum is carried through the surface per second in one direction as another. This demands an equality of pressure. Without analyzing the nature of the transition layer between a homogeneous gas and a homogeneous liquid it can be assumed that in the transition layer there is a continuous variation of density between the two phases. Furthermore, the vapor will be, for simplicity, treated as an ideal gas. As a result of the capillary forces at the surface such as Laplace and Van der Waals assumed, molecules in the transition layer will experience a force. This force is such as to hinder the evaporating molecules and to draw in the condensing ones. In order to analyze the problem further, it must be assumed that all molecules are alike, and that the volumes of the molecules can be neglected. It must also be assumed that Maxwell's distribution law holds for the molecules of the liquid as well as for the gas (see Chap. IV, Sec. 36).

From the principle of equality of mass assumed above (for equality in the number of molecules carried implies equality of mass transported for molecules all of one kind), the first equation may be set up. Assume the x-axis to be normal to the surface and call the velocity component along this axis u. The number of molecules with a velocity between u and $u + du$ is then given by Maxwell's distribution law as

$$\frac{N_D}{\alpha_D\sqrt{\pi}}\, e^{-\frac{u^2}{\alpha_D^2}}\, du,$$

where α_D is the most probable speed of the vapor molecules, while N_D is the number of molecules per cm³ of vapor. The number of molecules of this speed crossing a cm² of surface per second from the vapor phase is, then,

$$\frac{N_D}{\alpha_D\sqrt{\pi}} u e^{-\frac{u^2}{\alpha_D{}^2}} du.$$

In crossing the transition layer these molecules get an increase in kinetic energy of $\frac{1}{2}ms^2$ from the surface forces. Thus since all molecules moving in the direction of the surface will be aided in crossing the surface layer, the number of molecules of all speeds that cross is

$$\frac{N_D}{\alpha_D\sqrt{\pi}}\int_0^\infty u e^{-\frac{u^2}{\alpha_D{}^2}} du = \frac{N_D\alpha_D}{2\sqrt{\pi}}.$$

For the molecules starting from below the surface layer upwards there is the similar expression

$$\frac{N_F}{\alpha_F\sqrt{\pi}}\int_0^\infty u e^{-\frac{u^2}{\alpha_F{}^2}} du.$$

In this equation N_F represents the number of molecules in a cm^3 of the liquid phase and α_F the most probable speed of the liquid molecules. Whether α_F and α_D are the same can be left undecided for the present. Now the molecules that start outward have to do work against the surface forces in order to escape. Also, as they expand from the specific volume of the liquid phase to that of the gaseous phase, in escaping they must do work against the Van der Waals' $\frac{a}{v^2}$ forces if they are present. Both these amounts of work may be lumped into a single term, and this must be equivalent to saying that in escaping from the surface the molecules lose as much kinetic energy, on the average, as the condensing molecules gain. That is to say, they lose on the average an energy $\frac{1}{2}ms^2$. Thus only the molecules having speeds greater than the s of the $\frac{1}{2}ms^2$ out of the number above that start outward will be able to escape. The energy $\frac{1}{2}ms^2$ will, in fact be nothing other than the latent heat of vaporization per molecules, or $\frac{\lambda}{N_A}$, where λ is the heat of vaporization of a gram-molecule and N_A is the Avogadro constant. Thus the

number of molecules escaping from the surface per second, that is evaporating, is given by

$$\frac{N_F}{\alpha_F\sqrt{\pi}}\int_s^\infty ue^{-\frac{u^2}{\alpha_F^2}}du = -\frac{N_F\alpha_F}{2\sqrt{\pi}}e^{-\frac{s^2}{\alpha_F^2}}.$$

Since mass equilibrium exists, then, at once,

$$N_D\alpha_D = N_F\alpha_F e^{-\frac{s^2}{\alpha_F^2}}.$$

In an exactly similar manner the *energy* carried through the surface from both sides may be computed. In this case, however, the number transported must be multiplied by the energy transported in each case. Thus from the vapor side the energy transport for all velocities is given by

$$\frac{N_D}{\alpha_D\sqrt{\pi}}\int_0^\infty ue^{-\frac{u^2}{\alpha_D^2}}du \cdot \frac{1}{2}mu^2 = \frac{N_D m\alpha^3_D}{4\sqrt{\pi}}.$$

From the liquid side the energy transport per cm^2 per second into the layer is

$$\frac{N_F m}{2\alpha_F\sqrt{\pi}}\int_s^\infty u^3e^{-\frac{u^2}{\alpha_F^2}}du = \frac{N_F\alpha_F}{2\sqrt{\pi}}e^{-\frac{s^2}{\alpha_F^2}}\left\{\frac{1}{2}ms^2 + \frac{1}{2}m\alpha_F^2\right\}.$$

Of this energy $\frac{1}{2}ms^2$ is lost to the work of evaporation, thus the kinetic energy transported outward into the gas from the surface is

$$\frac{N_F\alpha_F}{2\sqrt{\pi}}e^{-\frac{s^2}{\alpha_F^2}}\frac{1}{2}m\alpha_F^2.$$

Equilibrium requires that

$$N_D\alpha_D^3 = N_F\alpha_F^3 e^{-\frac{s^2}{\alpha_F^2}}.$$

At the same time, however, it was also found that

$$N_D\alpha_D = N_F\alpha_F e^{-\frac{s^2}{\alpha_F^2}}$$

holds. These two statements can only be true *if* $\alpha_D = \alpha_F$.

It is also necessary to show that, in spite of the fact that only the molecules that have higher speeds can leave the liquid (for they lose energy in getting out) while all speeds can enter it, the Maxwell distribution is maintained on both sides (see Chap. IV, Sec. 43). This is proved if it can be shown that the one phase loses as many molecules of a given velocity per unit time as it gains from the other phase.

The number of molecules of velocity component normal to the surface between u and $u + du$ lost by the vapor phase in unit time is

$$\frac{N_D}{\alpha\sqrt{\pi}} u e^{-\frac{u^2}{\alpha^2}} du,$$

where $\alpha = \alpha_D$, the common speed. The number of molecules from the liquid phase which replaces these per cm² per second is

$$\frac{N_F}{\alpha\sqrt{\pi}} u_1 e^{-\frac{u_1^2}{\alpha^2}} du_1,$$

where u_1 is the velocity of the molecules leaving the liquid phase which are destined to have a velocity u on passing through the transition layer; that is, $u_1^2 - s^2 = u^2$. Substituting the value for u_1 gives at once

$$\frac{N_F}{\alpha\sqrt{\pi}} (u^2 + s^2)^{\frac{1}{2}} e^{-\frac{u^2+s^2}{\alpha^2}} \cdot (s^2 + u^2)^{-\frac{1}{2}} u du.$$

In order then that Maxwell's law be maintained, it is required that the expressions above be equal. Equating them, one has the condition as

$$N_D = N_F e^{-\frac{s^2}{\alpha^2}}.$$

That this condition is fulfilled follows at once from the equality of mass transfer which read

$$N_D \alpha_D = N_F \alpha_F e^{-\frac{s^2}{\alpha_F^2}},$$

provided $\alpha_D = \alpha_F = \alpha$, which is the case.

Finally, pressure equality requires that

$$N_F \alpha_F^2 e^{-\frac{s^2}{\alpha_F^2}} = N_D \alpha_D^2.$$

As this confirms the previous deduction, it is merely of passing interest and is given to show that all three conditions are mutually in agreement. The expression

$$N_D = N_F e^{-\frac{s^2}{\alpha^2}},$$

however, gives the equilibrium condition for evaporation. Now both N_D and N_F may be multiplied by m, the mass of a molecule, and each member of the ratio $\frac{s^2}{\alpha^2}$ by $\frac{N_A m}{2}$, where N_A is the Avo-

gadro number and m is the mass of the molecules. The equation then becomes

$$mN_D = mN_F e^{-\left(\frac{\frac{N_A m}{2} s^2}{N_A \frac{m}{2} \alpha^2}\right)}$$

But $\frac{N_A m}{2} s^2$ is nothing else than λ, the latent heat of evaporation per gram-molecule, while $\frac{N_A m}{2} \alpha^2$ is nothing else than RT, for $N_A \frac{m}{2} \alpha = N_A \frac{m}{2} \frac{2}{3} \bar{c}^2 = RT$. Also mN_D and mN_F are the densities of liquid ρ_D and gas ρ_F. One thus has

$$\rho_D = \rho_F e^{-\frac{\lambda}{RT}}.$$

This can be transformed readily into $\lambda = RT \log_e \frac{\rho_F}{\rho_D} = RT \log_e \frac{v_D}{v_F}$, where v_D and v_F are the molecular volumes of gas and liquid. This equation may also be deduced from thermodynamic reasoning. In the latter case it differs slightly, and this is due to the omission of certain factors in the kinetic theory deduction, which were omitted for the sake of simplicity (*i.e.*, the assumption of an ideal gas). The neglect of cohesive forces in the deduction would not change anything except that the $\frac{1}{2}ms^2$ would, as stated before, have to contain the work against the $\frac{a}{V^2}$ term of Van der Waals' equation. The neglect of the volumes of the molecules would play some rôle. The case was treated by Kamerlingh-Onnes.[55] The effect of the volumes of the molecules would result in a reduction of the number of the molecules starting outward which escape, due to the "shadowing" of the surface by molecules in the transition layer. In this case, however, the molecules struck by molecules which would escape are capable of escaping, so that the effect of the volumes of the molecules in this sense is negligible. Were foreign molecules present, this would not be so. However, a consequence of this must be considered. If a row of molecules normal to the surface be considered and one molecule with an energy u necessary for escape strikes the innermost one, the outermost one will receive

the necessary energy to escape if the impacts are perfectly elastic, central, and the masses are equal. Since, however, the rigidity of the molecules is great, the time taken for the end molecule to escape after the inner one is struck would be less than would have been the case for the initial molecule to have moved freely down the chain of molecules. If the time of travel of the molecular impulse through a molecule be negligible, then the time of escape by the "chain of impacts"* mechanism would be shorter. The time would be less in the ratio $\frac{u}{u + z\sigma}$, where u is the distance gone in 1 cm of free movement and $z\sigma$ is the length of path covered inside the molecules lying in the path u cm long, there being z molecules in the row of u cm length in the gas and σ being the diameter of a molecule. If the collisions of all sorts be averaged as well as relative motions, analysis yields the apparent velocity of the molecules as $u \frac{v}{v - b}$ where v is the volume of the gas and b is the Van der Waals' b (see Sec. 49) Chap. V). The change in the theory above produced by the use of $u\left(\frac{v}{v - b}\right)$ in place of u gives as a final equation

$$N_D \frac{v_D}{v_D - b_D} = N_F e^{-\frac{s^2}{\alpha^2}} \frac{v_F}{v_F - b_F},$$

which gives

$$e^{\frac{\lambda}{RT}} = \frac{v_D - b_D}{v_F - b_F},$$

or

$$\lambda = RT \log \frac{v_D - b_D}{v_F - b_F}.$$

This equation is in perfect agreement with the thermodynamically deduced equation for condensation. In practice, however, it is simpler to use the approximate equation for an ideal gas.

It is now possible to take up the considerations of Frenkel.[43] In taking up his discussion it is perhaps best to preface it with the statements that Frenkel assumes that *all* cases of impacts between surfaces and molecules result in condensation and reevaporation. It is doubtful whether in the case of gases like H_2 on surfaces

* This "chain of impacts" mechanism is not a new concept. It was used by Jaeger in his treatment of the evaluation of the b of Van der Waals' equation, of Sec. 49. The treatment there is not given but is referred to.

covered with an adsorbed film of H_2, or of gas molecules with certain oil and other surfaces where slip is observed, this dogmatic assertion can be made. It is also doubtful if it is essential to the theory. It is probable that in a large number of instances the surface forces act and the theoretical treatment may be strictly applied. Where forces are weak, it is conceivable that Frenkel's time of condensation becomes identical with the time of a molecular impact. Such a case would give the ordinary diffuse reflection if the surface was completely molecularly rough (Maxwell's $f = 1$), and a certain amount of specular reflection where this is not the case. With this caution based on a broader point of view than that of Frenkel, his treatment of the subject may be taken up.

He assumes that the atoms or molecules strike the surface, condense, and reevaporate after a time. The duration in the condensed state, obviously, must vary greatly, depending on the temperature of the surface and on the affinity between the molecules and the surface. If the number of molecules striking unit surface in unit time is small, or if the duration of the condensed state is short, the surface will be covered with a relatively diffuse monomolecular layer. As equilibrium between reevaporation and condensation sets in, one will then have a layer of constant surface density under the given conditions. Call n the number of adsorbed atoms per cm², and ν the number of atoms striking unit surface in unit time. One may then write as a first approximation that $\nu = \alpha n$. Here α is a constant whose dimensions are $\frac{1}{T}$. As used, it measures the velocity of sublimation, or, perhaps better, the probability of sublimation of an adsorbed molecule, for αdt represents the chance that in dt a molecule will leave the surface. In taking the reciprocal of $\frac{1}{\alpha} = \tau$, τ is now a time which defines the average time in the condensed state. As the admirable German expression for this, the time of lingering, *verweilzeit,* expresses the meaning more tersely than any English equivalent, the time τ will hereinafter be termed the *verweilzeit*

If one ceased bombarding the surface with molecules, the molecules should, after a given time, reevaporate. The rate of evaporation would be given at once by the relation

$$dn = -\alpha n dt$$

from the definition of α above. Hence $\frac{dn}{dt} = -\alpha n$, and if $n = n_o$ at $t = 0$ integration gives at once that

$$n = n_o e^{-\alpha t}, \text{ or } n = n_o e^{-\frac{t}{\tau}}.$$

The above relation was deduced only for small values of n. If ν is large or if τ is very large, the stationary state which would give a constant n is not reached, for then molecules would accumulate faster than they could evaporate. When the number adsorbed had reached a critical value n_K, a part of the surface would be covered by a monomolecular layer. Further, condensation would then not occur on the initial surface, but on the newly adsorbed surface where the forces with metals would be greater than before. Thus condensation at this point would begin and the solid deposit observed by Wood would be forming. Langmuir[56] actually studied the formation of such layers. Wood had shown that Cd vapor would not condense to a visible deposit on glass unless the latter was cooled to liquid-air temperatures. Langmuir modified this by cooling a portion of the glass to liquid-air temperatures for too short a time for a visible deposit to form. If heated to room temperature, a visible deposit formed when the Cd vapor was shot against the spot. He further showed that condensation was more rapid on surfaces that were not allowed to warm up completely after being cooled before the stream of vapor was turned on them. This he ascribed to atoms that had condensed, but in such a form that they could not remain on the warmer surface, owing to evaporation. On the theory developed in his *Physical Review* article, deposits containing contiguous pairs or more of atoms could not evaporate at room temperatures, while single atoms readily did. He also observed that if one-half of a bulb filled with Cd in that half were heated in an oil bath, a foggy condensation occurred over the unheated surface even when liquid air had not been used. This condensation consisted of isolated groups of crystals. This fact he uses as an argument against Wood's reflection theory, for he states that on Wood's theory no deposit should have occurred. He ascribes the difference between this experiment and Wood's unidirectional stream-reflection experiments to the increased density of the vapor. It is doubtful whether the conditions of the stream density were sufficiently well known relative to those in Wood's experiments to make such an assertion. The experiments do,

however, indicate the nature of the effect of atoms or molecules present in stimulating further condensation, though why the isolated condensation should occur here is not clear. Calculation shows that the deposit formed on the surface cooled by liquid air for 1 min. only, from Cd at 60°, contains only enough Cd to cover $3/1000$ of the surface with Cd atoms at room temperature. Yet such a film will serve as a nucleus for further condensation to a visible deposit.

It is seen from the experiments of Langmuir that n_K need not mean a uniform monomolecular layer covering the whole surface, but a layer sufficiently dense so that the chance of atoms coming together in groups of two or more is great enough to cause the deposit to form on atoms of the same metal. For each ν there will be a critical temperature T_K at which the average *verweilzeit* τ will be great enough so that a layer of the critical thickness n_K forms. At $T > T_K$ the temporary layer discussed before is formed, which evaporates rapidly after cessation of the stream.

In metals and glass, where the metal does not "wet" the glass, the adhesive forces are less than the cohesive forces. Thus the reflection or reevaporation occurs for the glass surfaces, but not for metallic surfaces at room temperatures. On the other hand, phenomena at low pressures, such as the removal of gases, surface catalysis, etc., indicate that many of the gases form powerfully adhering monomolecular films on the surfaces of metals and glass. These films saturate the surface forces of the metals. The residual forces between the gas-coated surface and the bombarding gas molecules are very weak, for the intermolecular forces between molecules of the so-called permanent gases are very weak. The result is that the *verweilzeit* may become negligible and there seems no reason, judging from the values of f and a in some gases, that these forces cannot be completely neglected as Baule does. This viewpoint is strenuously attacked by Frenkel in his article, without adequate reasons being given. It is, however, possible to accept his treatment with this reservation, and to consider both types of reflection and condensation in reevaporation as occurring under proper circumstances.

Quantitatively, Frenkel proceeds as follows: Assume a layer of adsorbed particles small in number compared to a uniform monomolecular layer and in equilibrium with a gas phase which contains n' molecules of the same sort. Equilibrium will then be represented by the equation

$$\nu = \alpha n = \frac{1}{\tau}n.$$

Here ν is the number of molecules striking the surface of the body s in unit time, and is given by $\nu = \frac{s}{2V}n'\bar{v}$, where V is the volume of the gas and $\bar{v}$ the average of the velocity component normal to s. If Maxwell's distribution be assumed, the $\bar{v}$ used is given by

$$v = \frac{\int_0^\infty ce^{-\frac{mc^2}{2kT}}dc}{\int_0^\infty e^{-\frac{mc^2}{2kT}}dc} = \sqrt{\frac{2kT}{\pi m}}$$

whence

$$\nu = \frac{sn'}{V}\sqrt{\frac{kT}{2\pi m}}$$

From the discussion of the equation for the evaporation, one may take the expression deduced that

$$N_D = N_F e^{-\frac{s^2}{\alpha^2}}.$$

Here N_D is the number of molecules per cm^3 of vapor in equilibrium with a liquid where there are N_F molecules of the liquid per cm^3. The deduction holds in the case of equilibrium at a surface layer equally well. For this purpose multiply top and bottom of the expression $\frac{s^2}{\alpha^2}$ by $\frac{m}{2}$, and replace N_D by $\frac{n'}{V}$ and N_F by its equivalent $\frac{n}{s\delta}$ where δ is the thickness of the adsorbed layer. Then $\frac{\frac{ms^2}{2}}{\frac{m\alpha^2}{2}}$ is the ratio of the kinetic energy necessary for escape from the surface u_o (*i.e.*, the potential energy of the adsorbed molecule) to the average kinetic energy of agitation of the gas and surface molecules at a temperature T. This latter energy is kT in the Boltzmann notation. Thus the following relation may be written between n and n':

$$\frac{n'}{V} = \frac{n}{s\delta}e^{-\frac{u_o}{kT}}.$$

or

$$\frac{n}{s} = \frac{n'}{V}\delta e^{\frac{u_o}{kT}}.$$

A more satisfactory insight into the problem can be arrived at as follows, for δ is unknown and tells nothing about the forces acting. Assume the adsorbed molecule to be bound in its position at the surface by forces which enable it to oscillate normal to the surface s with a period τ_o. In this case the elastic force acting on a molecule displaced a distance z is $z\frac{4\pi^2}{\tau_o^2}m$ in terms of its period, mass, and displacement. For small values of z the potential energy is $\Delta u = \frac{2\pi^2}{\tau_o^2}mz^2$. Now the value of δ can be obtained from this, for δ is the thickness of a layer within which the center of the molecules adsorbed must lie. This average displacement δ is obtained from the number of molecules out of N that have a displacement z multiplied by dz and integrated over all distances that bind the molecules in the layer, divided by the number of molecules N. Now the molecules having the displacement z are those that have an energy of oscillation Δu characteristic of z as given by the Maxwellian distribution law. This is $e^{-\frac{\Delta u}{kT}}$, and hence

$$\delta = \frac{N\int_A^B e^{-\frac{\Delta u}{kT}}dz}{N}.$$

The limits A and B are dependent on the forces and complicate integration. Frenkel assumes that, since $e^{-\frac{\Delta u}{kT}}$ decreases so rapidly as z increases, one may integrate for z from $-\infty$ to $+\infty$. Thus

$$\delta = \int_{-\infty}^{+\infty} e^{-\frac{2\pi^2 m}{\tau_o^2 kT}z^2}\,dz = \tau_o\sqrt{\frac{kT}{2\pi m}}.$$

It therefore follows at once that

$$\frac{n}{s} = \frac{n'}{V}\tau_o\sqrt{\frac{kT}{2\pi m}}e^{\frac{u_o}{kT}}. \tag{3}$$

He shows that at very low temperatures quantization of the energy must be used, and obtains an expression for n

$$n = \frac{n'}{V}\frac{n_o h^3 e^{\frac{u_o}{kT}}}{(2\pi mkT)^{3/2}},$$

where h is the Planck constant and n_o is the number of molecules in the adsorbing layer. This is of little but passing interest,

and shows that even here quantum theory may be profitably used. If it is remembered that

$$\nu = \frac{sn'}{V}\sqrt{\frac{kT}{2\pi m}} = \frac{1}{\tau}n$$

then

$$\frac{n}{s} = \frac{\tau sn'}{V}\sqrt{\frac{kT}{2\pi m}} = \frac{n'}{V}\tau_o\sqrt{\frac{kT}{2\pi m}}e^{\frac{u_o}{kT}}$$

or

$$\tau = \tau_o e^{\frac{u_o}{kT}}.$$

Thus one has τ, the average *verweilzeit*, expressed as the period of oscillation of the molecule in the adsorbed layer, the potential energy in the layer, and the absolute temperature.

While the formula was deduced for the case of a diffuse monomolecular layer, it can hold also for any layers. In order to adapt it to this case it becomes necessary to alter u_o and τ_o to fit the new conditions. If the particles are unequally spaced, the values of u_o and τ_o will be different for different particles, depending on their proximity to other particles. This will be a very important factor for cases such as that of Cd on glass investigated by Langmuir, that is, for cases where cohesion is far greater than adhesion to the surface. Call the work function or energy function of an atom which is *combined* with i atoms of the same sort u_i and its *verweilzeit* τ_i. The term "combined atoms" or atoms combined with other atoms comprises such atoms as are closer than a distance d_o from each other, which will be termed the "effective atomic diameter." All atoms greater than d_o distant from other atoms may be termed "isolated."

Call the extra work to separate an atom combined with one other atom Δu_1, then u_i may be assumed to be given by $u_i = u_o + i\Delta u_1$, and accordingly, the time τ will become $\tau^{(i)}$ defined by the relation

$$\tau^{(i)} = \tau_i e^{\frac{u_o + i\,\Delta\,u_1}{kT}}$$

Here $\tau^{(i)}$ is the average *verweilzeit* of an atom surrounded by i neighbors.

Let it be assumed that the number n of atoms which constitute the surface is small compared to the number n max. that would form a complete monomolecular layer. If they are distributed completely at random, then all combinations and distributions will be possible if the surface is large enough. The probability

that an atom of such a distribution is closer than the distance d_o to another of the $n - 1$ atoms left would roughly be given by the relation $(n - 1) \frac{\sigma_o}{s}$, where σ_o, the effective surface occupied by an atom, is $\sigma_o = \pi d_o^2$. This expression is only an approximation, as some of these areas σ_o may overlap. It is the less the smaller the total number n. Thus for small values of n, the number of isolated atoms will be

$$n_o = n\left[1 - (n - 1)\frac{\sigma_o}{s}\right],$$

and the number of combined ones will be $n_1 = n(n - 1) \frac{\sigma_o}{s}$. It may be assumed, for simplicity, that, although the number of molecules in a combined group has not been computed, the probability for more than two being combined under the above circumstances is small. Thus in this case one deals largely with pairs, or twins. This is the viewpoint also used by Langmuir.[57]

Frenkel further assumes that it is not merely chance that causes the pairing of the atoms. He assumes that their cohesive forces tend to further this. Since the movement along the surface requires no energy, the atoms at the surface can be considered as a two-dimensional gas of diatomic molecules that is largely dissociated. The work of dissociation is Δu_1. The ratio of the number of the pairs associated as a result of the forces, relative to those associated by accident, will be given by the ratio of $e^{\frac{\Delta u_1}{kT}}$ to 1. He therefore modifies his equation to suit this by setting for σ_o the area $\sigma = \sigma_o e^{\frac{\Delta u_1}{kT}}$. Calling $n - 1$ equal to n, for n is large compared to unity, then n_1, the number of condensed associated atoms, is given by $n_1 = \frac{n^2\sigma}{s}$. The $n - n_1$ atoms may be considered as isolated.

Whether the last calculation assuming the surface atoms to be in the state of a two-dimensional gas is legitimate is questionable. It would seem, in fact, surprising with the intense forces between atoms that under these conditions condensation would not always take place, if once two atoms could get together. If Langmuir's interpretation of his general condensation on an uncooled surface were correct, this process would greatly aid it. At any rate, it gives a basis for further discussion.

If now the probability of evaporation of an isolated atom be $\alpha = \frac{1}{\tau}$ and of a combined one be $\alpha' = \frac{1}{\tau'}$, the sum of the adsorbed atoms leaving in a time dt will be $(\alpha n_o + \alpha' n_1)dt$. If ν represents the number of atoms that strike the surface s in unit time, the differential equation for n becomes

$$\frac{dn}{dt} = \nu - \alpha n_o - \alpha' n_1.$$

As $n_1 = \frac{n^2\sigma}{s}$, and if $(\alpha - \alpha')\frac{\sigma}{s}$ is called β, where $\beta > 0$, then

$$\frac{dn}{dt} = \nu - \alpha n + \beta n^2.$$

For the case of equilibrium $\frac{dn}{dt} = 0$, and

$$n = \frac{\alpha - \sqrt{\alpha^2 - 4\beta\nu}}{2\beta}.$$

The other possible value for n, $n = \frac{\alpha + \sqrt{\alpha^2 - 4\beta\nu}}{2\beta}$, has no physical meaning, for with $\nu = 0$ it would give $n = \frac{\alpha}{\beta}$, while n must be 0 when $\nu = 0$. Again, only as long as $\alpha^2 \geq 4\beta\nu$ is n real. At the critical value $\alpha^2 = 4\beta\nu$, $n = \frac{\alpha}{2\beta}$, and the particular critical state is determined by ν reaching a value $\nu_k = \frac{\alpha^2}{4\beta}$. If ν becomes greater than ν_k the quantity n becomes imaginary. This means that the equilibrium assumed does not exist. The density of the layer must continue to increase, and one has the case of the condensation of the metal on the metal surface. Now ν_k is a function of the temperature, since both α and β are functions of temperature, and, reciprocally, the critical temperature at which this condensation occurs is a function of ν when ν approaches $\frac{\alpha^2}{4\beta}$, or specifically when $\nu = \frac{\alpha^2}{2\beta}$ the critical temperature varies with ν.

The relation between T and ν can be easily found from the preceding equations, as

$$e^{\frac{u_1}{kT}}\left(1 - \frac{\tau_o}{\tau_1}e^{-\frac{\Delta u_1}{kT}}\right) = \frac{s}{4\sigma_o\nu\tau_o},$$

where τ_1 is the period of atoms bound in a pair and τ_o is the period for isolated atoms, while Δu_1 is the work to separate a pair, and u_1 is the work to remove an atom of a pair from the surface.

At the critical temperature the density of the adsorbed layer reaches its maximum value which can exist in equilibrium. This thickness is given by the relation $n_k = \frac{\alpha}{2\beta}$, the value of n at ν_k. Hence

$$\frac{n_k}{s} = \frac{\alpha}{2\beta s} = \frac{s}{s\left(1 - \frac{\alpha'}{\alpha}\right)\sigma} = \frac{1}{2\sigma_o\left(1 - \frac{\tau_o}{\tau_1} e^{-\frac{\Delta u_1}{kT}}\right)}.$$

This value of the critical density is distinctly less than that which would be demanded by the densest covering possible on the surface, for if it is assumed that each atom of diameter δ_o can be surrounded by six other atoms, the minimum surface will be $\frac{\sqrt{3}}{2}\delta_o^2 = 0.87\delta_o^2$. On the other hand,

$$\frac{s}{n_k} = 2\sigma_o\left(1 - \frac{\tau_o}{\tau_1} e^{-\frac{\Delta u_1}{kT}}\right),$$

and, as $\sigma_o = \pi d_o^2$, one has

$$\frac{s}{n_k} = 2\pi d_o^2\left(1 - \frac{\tau_o}{\tau_1} e^{-\frac{\Delta u_1}{kT}}\right).$$

If d_o is nearly equal to δ_o, and if $\frac{\tau_o}{\tau_1} e^{-\frac{\Delta u_1}{kT}}$ is small compared to unity, it is seen at once that the area per atom in the critical layer is about 1/7 that of the densest possible monomolecular layer. Again, if the atoms were uniformly distributed, the distance between any two atoms would be $\sqrt{2\pi} d_o$, and as d_o is required so that atoms may further condense, no condensation would take place. Thus the pairing is essential for condensation, and these serve as nucleii.

Isolated atoms play no *direct* rôle in the phenomenon. They do, however, increase the chance of pair formation and thus aid condensation. Of course, strictly, larger complexes also build up which are not included in the theory. As a first approximation, however, the equations give the situation up to near the critical point. Again, one may also neglect $\frac{\tau_o}{\tau_1} e^{-\frac{\Delta u_1}{kT}}$ to a first

approximation with respect to unity. This enables a qualitative test of the theory to be made.

From the experiments of Chariton and Semenow[45] quoted, the critical temperature of Cd on a surface of picene for $\nu = 2 \times 10^{17}$ per cm^2 is 203°K. When ν calculated for the edge of their plate was reduced by half, the decrease in temperature to cause condensation as estimated from the curvature of the line of condensation and the temperature gradient was 5°.

If one write

$$e^{\frac{u_1}{kT}} = \frac{s}{4\sigma_o\tau_o\nu},$$

then

$$u_1 = k\frac{T_1T_2}{T_2 - T_1}\log_e\frac{\nu_2}{\nu_1}.$$

If the energy u_1 corresponds to gram-calories per gram-atom, $k = R = 2$ cal. Putting in Chariton and Semenow's values for ν_2, ν_1, T_2 and T_1, one arrives at $u_1 = 11{,}000\ \frac{\text{cal.}}{\text{mol.}}$. This is the work of evaporation for paired atoms, and in order of magnitude it approaches the heat of sublimation but is somewhat less (*e.g.*, these heats for Na, K, and Cd are 26,000, 23,000, and 32,000 $\frac{\text{cal.}}{\text{mol.}}$).

Placing u_1 in the equation

$$\sigma_0\tau_0 = \frac{s}{4\nu}e^{-\frac{u_1}{kT}},$$

and assuming $\nu = 2 \times 10^{17}$ at $T = 203$°K., then $\sigma_o\tau_o = 2.5 \times 10^{30}$. As the order of magnitude of σ_o is 10^{-16} cm^2, then $\tau_o = 10^{-14}$ sec. In solid bodies the period of oscillation is of the order of 10^{-13} sec. This is a rough agreement. That it comes out too low may be due to the fact that the value taken for u_1 was too high, as $\frac{\nu_2}{\nu_1}$ was inaccurately known. If $\frac{\nu_2}{\nu_1}$ had been 1.9 instead of 2, u_1 would have been 10,200 gram-cal., and τ_o would have been 10^{-13} sec. The average thickness δ of the layer under these conditions would have been 10^{-9} cm.

One more case of interest is the adsorption of a gas film. Here the molecules do not stick together but cling to the surface, and thus decrease the effective area of the surface which is available for further adhesion.

Let σ_o be the surface occupied by one molecule, and thus screened off from the other molecules. If n molecules are adsorbed on s, then of the ν molecules striking only $\nu\frac{s - n\sigma_o}{s} = \left(1 - \frac{\sigma_o}{s}n\right)$ will be able to adhere. If τ is the average *verweilzeit* the condition for equilibrium will take the form

$$\nu = \left(1 - \frac{\sigma_o}{s}n\right) = \frac{n}{\tau}.$$

Thus

$$n = \frac{1}{\frac{\sigma_o}{s} + \frac{1}{\tau}}.$$

Remembering that

$$\tau = \tau_o e^{\frac{u_0}{kT}}$$

and that

$$\frac{n}{s} = \frac{n'}{V}\tau_o\sqrt{\frac{kT}{2\pi m}}\, e^{\frac{u_0}{kT}},$$

while $p = \frac{kn'T}{V}$, one obtains for the thickness of the layer as a function of temperature and pressure the relation

$$\frac{s}{n} = \sigma_o\left(1 + \sqrt{\frac{2\pi mkT}{p\sigma_o\tau_o}}\right)e^{-\frac{u_0}{kT}}.$$

This shows that at sufficiently low temperatures n approaches the value $\frac{s}{\sigma_o}$ which it would have for a surface completely covered by a monomolecular layer. At these temperatures considerable changes of pressure are of little effect, for the $\frac{p\sigma_o\tau_o}{\sqrt{2\pi mkT}}$ is negligible. The pressure begins to exert an influence when

$$\frac{\sqrt{2\pi kmT}}{p\tau_o\sigma_o}\, e^{-\frac{u_0}{kT}}$$

approaches unity.

Thus Langmuir's experiments show that a compact monomolecular layer of air molecules on W begins to disappear only at 3000°K., at pressures of the order of 1 dyne-cm. Assuming that

$$\frac{1}{\tau_o\sigma_o}\,\frac{\sqrt{2\pi mkT}}{p}\, e^{-\frac{u_0}{kT}}$$

is about unity at $T = 3000°$K., if τ_o be assumed 10^{-13}, $\sigma_o = 10^{-16}$, p about 1 dyne per cm², $k = 1.3 \times 10^{-16}$, and $m = 5 \times 10^{-23}$, then $e^{-\frac{u_0}{kT}}$ is about 10^{-12}. This gives u_o as about 170,000 cal. per molecule. This value is pretty high, as the heat of sublimation of W is 150,000 cal. It is, apparently, of the right order of magnitude. The calculation is, however, only rough, as the diffusion of the gas into the solid, the complexity of the gas, and the presence of chemical reactions complicate it. It is interesting to see that it leads to the proper order of magnitude at least.

The discussion shows that, although the theory is still very rough, a clearer insight into the relation of molecules and solid surfaces is gained by the study.

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CHAPTER VIII

THE REALITY OF MOLECULAR MOTIONS, BROWNIAN MOVEMENTS

85. Introduction.—In the preceding seven chapters the kinetic concept of a gas and its consequences was developed in some detail, and the development in many cases resulted in predictions which were more or less successfully verified by experiment. Thus in more recent years the predicted velocities of silver atoms, the distribution of velocities, and free paths were roughly measured and found to be in agreement with the theory. Furthermore, the representation of the various constants of transfer discussed in Chap. VI in terms of the kinetic theory at an early date furnished strong indications of the correctness of the assumptions of the kinetic hypothesis. However, while these predictions were fulfilled, until 1908 no direct proof of the fundamental assumption of the kinetic theory existed; to wit, no proof of the continuous and eternal heat motions of the molecules was known. To place the kinetic hypothesis on the basis of a proper theory, such a proof was absolutely essential, and it was due to the lack of this evidence that the proponents of the school of energetics (see Chap. I) had a legitimate foundation for their criticism of the kinetic conception of gases.

Again, before 1908, there was no direct means of estimating the Avagadro or Loschmidt's number N, that is, the number of molecules in a gram-molecule or in a cm^3. It is true that the quantities N and σ, the molecular radius, were bound together in the equation for the mean free path, $L = \dfrac{1}{\sqrt{2}\pi\sigma^2 N}$, and it is clear that if σ could be evaluated N could be determined. Previous to this date attempts had been made to evaluate σ from the limiting thickness of soap-solution films just before they break[1] (*i.e.*, where the film was supposed to be two molecules thick), and from the value of Van der Waals' b.[1] The first method gave very crude and uncertain results of the order of ten times the value of σ obtained from b taken from the critical data. Clearly then, it

remained for a direct determination of N, and a direct proof of the heat motions of the molecules to establish the kinetic hypothesis on the firm basis of an acceptable theory.

These conditions were realized at one stroke through the genius of the French physical chemist, Jean Perrin,[2] in 1908, by a study of the Brownian movements. By means of these movements by two independent lines of reasoning, based on the assumptions that they were the result of molecular motions, Perrin was able to obtain a value of N in good agreement with the value of N calculated from σ from the critical data. The value of N thus obtained was also in satisfactory general agreement with the early rough values of N obtained by Millikan[3] and Rutherford[4] from Ne and the value of e the unit electric charge by entirely different means. The agreement of observations on the Brownian movements with the equations derived, assuming them to be the result of molecular impacts, definitely established the real existence of the assumed heat motions. Later experiments of Millikan and Fletcher[5] using minute electrically charged oil drops in air giving an accurate value of the Faraday constant Ne verified the assumptions in a still more striking manner. The theory and the results of these measurements will constitute the body of this chapter.

86. Brownian Movements.—In 1827, an English botanist, Brown, observed that in aqueous suspensions of fine inanimate spores the spores were apparently in constant motion dancing hither and thither in the field of the microscope without apparent rhyme or reason. He extended his observations to suspensions of a large number of other inorganic substances, the so-called colloidal solutions, and found it to be a general phenomenon. His observation of the motions lead him to venture the idea that the motion was due to the unequal bombardment of the particles on various sides by the molecules of the liquid executing their heat motions and that they were therefore a manifestation of molecular heat motions. This started a violent controversy and a long line of experimental investigations by now nearly unknown investigators which definitely terminated only with the quantitative experiments of Perrin. The investigations preceding the work of Perrin established the following facts, which in a qualitative fashion pointed quite strongly to the correctness of the tentative explanation of Brown. These facts are as follows:

1. The motions are completely irregular and random. No two particles in one locality are moving in the same direction at the

same time. The motions are also independent of the location of the particles in the observation chamber. Thus they cannot be due to eddy, convection, or streaming motions in the liquid.

2. They are independent of jarring or shaking of the vessel.
3. The lower the viscosity of the liquid the faster the motion.
4. The smaller the particles the greater the motion.
5. Two particles the same size move equally fast at the same temperature.
6. The motions are continuous and eternal, that is, the colloidal quartz particles in the liquid suspensions included in certain quartz specimens that are thousands of years old still show the Brownian movements. Thus these cannot be attributed to special types of physical activity, such as is displayed by camphor on a clean water surface, for such actions cease after a short interval of time.

These results indicate first that the motions are properties of individual particles, that each one of these acts independently, and that local convection currents, streaming, and mechanical agitation are not the cause of them. The variation of the motion with size, viscosity, and temperature is in agreement with the concept that they are due to unbalanced forces of the molecular type. Finally, the eternal nature of the motion suggests that the energy cannot come from the chemical or electrical properties of the suspension and the only source of energy of this duration is the ever-present heat motion of the liquid molecules.

Accepting Brown's hypothesis then, the following picture of the processes at work may be drawn. The suspended particles, large compared to the molecules of the liquid (perhaps millions of times larger) are being continually bombarded on all sides by molecules of the liquid executing their heat motions. If the particles are sufficiently large, on the average, equal numbers of molecules strike them on all sides each instant. For smaller particles, from the laws of chance, the numbers striking various sides each instant may not be equal. Thus the particle at each instant suffers an unbalanced force due to the inequality in the number of molecular impacts on different parts of the surface. The result of such an action is a force causing the particle each instant to move this way or that in response to the force, its motion being opposed by the viscous drag of the liquid. Thus the particles act just like very large molecules in the liquid and the motions they exhibit should be exactly analogous to the real motions of the molecules.

It is this similarity of these large observable particles to molecules that Perrin used as the basis of one of his proofs, for if these particles differ from molecules in their behavior in respect to heat motions just in size, they should obey the laws of partial pressures and of molecular atmospheres. Also if the particles are moved hither and thither by the unbalanced forces of the liquid, the mathematical theory of the amplitude of their motion in a given time for particles acted on in the fashion deduced by von Smoluchowski and later independently by Einstein should be applicable to this case, and the dependence of the amplitude on various factors, such as temperature, size, and viscosity, should be in accord with that observed. The test of this equation constitutes the second of Perrin's methods of attack and it will be the task of the next two sections to derive the relations and indicate the success of the measurements.

87. Brownian Movements and the Law of Atmospheres.—The study of the physical chemistry of solutions has shown that molecules of dissolved substances in a liquid behave in many respects as if the same molecules were moving freely as gas molecules in empty space. Thus the molecules of 342 grams, (*i.e.*, 1 gram-molecule), of cane sugar dissolved in 22.4 liters of solution act very much as if they were molecules of sugar vapor at a pressure of 1 atmosphere at the existing temperature, that is, they execute heat motions and exert a partial pressure on the walls, commonly known as the osmotic pressure. By using heavier molecules than sugar, the case is not altered, for there is no change in the observed laws with molecular weight. There is no reason why the molecules to be discussed, even if they have the size of colloidal protein molecules visible as diffraction patterns in the ultra-microscope, should not show exactly the same behavior as sugar solutions of low molecular weight.* It is, therefore, not

* It appears now that, in spite of the views of certain colloidal chemists, colloidal particles in suspension do not differ essentially from crystalloidal particles in solution. Their chief difference lies in their greater size, which makes them unable to pass through certain filters and which also enables them to scatter light. They are also at times electrically charged, the charge being very active in preventing agglomeration and precipitation. Certain crystalloidal solutes (the ions), however, also exhibit charges in solution whose nature may not be very different from that of the particles above. They also follow the laws of osmotic pressure. It is possible that the charges on Perrin's particles might have affected his results. Apparently, he chose particles where this was not the case. That he did so is evidenced by results of later workers who could not check *some* of his results.

unlikely that the laws of solutions and hence of gases are justifiably applicable to suspensions of colloidal particles in liquids. It was this analogy which lead Perrin to the first of his considerations.

Assuming that the colloidal particles in a suspension may be compared to an atmosphere of molecules in free space, say the nitrogen molecules of the atmosphere, it is possible to proceed as follows. The nitrogen molecules of the earth's atmosphere are in constant heat motion. Due to this, they are moving equally in all directions. At the same time they are acted on by gravity. Accordingly, those in the outer layers have a resultant force urging them towards the center of the earth, that is, there is a pressure exerted by them on the next inner layer of molecules. These, in turn, are attracted inwards, and they add the force of attraction upon themselves to the pressure exerted on them by the outer layer. Through their heat motions the pressure is transmitted from layer to layer of the gas, becoming continually greater as the center of the earth is approached. Since the pressure acting from above increases the density of the gas, more molecules are crowded into each successive layer than there were in the layer before. Hence the attractive force on an inner layer will be greater than on the next outer one and the pressure will increase more rapidly than by a linear law with the decrease in distance from the center. Also, the heavier the gas molecules the greater the gravitational force on each layer, and hence the more rapidly the pressure will increase with decreasing distance from the center. Thus for nitrogen there is an atmosphere like that of the earth—tenuous outside, dense at the surface. For molecules like sugar that are some 10 times heavier than nitrogen it would be necessary only to go up a distance $e^{1/10}$ as high to reach the same fractional density as is exhibited by the atmosphere. For colloidal particles whose mass may be 10^5 times that of the sugar molecules the fractional change in density, which in the atmosphere requires kilometers in height, will occur in millimeters in colloidal suspensions. Thus if the colloidal particles showing Brownian movements act exactly as if they were large molecules, their motions being due to the heat motions of the molecules of the liquid, a colloidal suspension should show a change in density for different layers depending on the mass of the particles, but exactly analogous in form to the changes in density of the earth's atmosphere. To study this, the law of atmospheres, which was originally due to Laplace, must be deduced.

Consider a cylinder of gas of cross-section a and also one of the layers mentioned above dh cm high. Call the pressures on its bottom and top p and p'. Then $p > p'$, for the mass of the layer dh acted on by gravity has been added to p' to make p. Thus $p - p' = \frac{(a)(dh)\rho g}{a}$. This merely says that the force of gravity $a\ dh\rho g$ acting on the gas divided by the area a is the difference in pressure $p - p'$. Here g is the constant of gravity and ρ is the density of the gas in grams per cm³. Hence

$$dp = p - p' = -dh\rho g = -\frac{Mgdh}{v},$$

the $-$ sign indicating that as h increases p decreases. Here M is the mass of a gram-molecule of gas, and v the corresponding volume $\left(i.e., \rho = \frac{M}{v}\right)$. Since it was assumed that the Brownian particles act like nitrogen molecules, it is legitimate in the rough calculations to follow to assume that Boyle's law holds. Then for such particles as for N_2 one may approximately write $pv = R_AT$, where v and R_A refer to a mol, and one has

$$dp = -\frac{Mgdh}{\frac{R_AT}{p}}$$

or

$$\frac{dp}{p} = -\frac{Mg}{R_AT}\,dh.$$

Integrating this from $p = p_0$ at $h = 0$, to $p = p$ at $h = h$,

$$\int_{p_o}^{p}\frac{dp}{p} = -\frac{Mg}{R_AT}\int_0^h dh, \quad \log p - \log p_o = -\frac{Mg}{R_AT}\,h$$

$$p = p_o e^{-\frac{Mg}{R_AT}h}.$$

Further, since the number of particles or molecules per cm³, n_o and n, are proportional to p_o and p, respectively,

$$n = n_o e^{-\frac{Mg}{R_AT}h}.$$

This is Laplace's well-known law of atmospheres and it expresses precisely how the number of particles or molecules per unit volume will vary with distance from the earth's surface. The

equation may be modified a bit further by replacing M, the gram-molecular mass, by mN_A, the mass of a single particle times the number in a gram-molecule, hence

$$\frac{n}{n_o} = e^{-\frac{mN_A gh}{R_A T}}.$$

Thus the density of particles increases exponentially as the height decreases. The rate of increase is greater the greater the mass m of the particles, and the lower the temperature. If the values of m, g, h, R, and T were known for a given $\frac{n}{n_o}$ and h, N_A, the Avogadro number, could be found.

In the colloidal particles in solution the force of gravity acts on the particles which are buoyed up by the liquid in which they are suspended. Thus mg must be replaced by $m\left(\frac{D - d}{D}\right)g$, where d is the density of the liquid and D is the density of the particles. If V is the volume of the particles, then

$$\frac{n}{n_o} = e^{-\frac{N_A}{R_A T}m\left(1 - \frac{d}{D}\right)gh}$$
$$= e^{-\frac{N_A}{R_A T}V(D - d)gh}.$$

In the logarithmic form this becomes

$$\log\frac{n_o}{n} = \frac{N_A}{R_A T}V(D - d)gh.$$

To test this experimentally, Perrin used colloidal suspensions of gum mastic and of gum gamboge. These could be prepared by dissolving the gum in alcohol and then pouring the clear solution into water. In this way clear spherical globules of the substances appeared, of which the smaller ones showed the Brownian movements very nicely. The equation to be tested, however, demands the V or m for all the particles considered be the same. To insure this, Perrin separated particles of one size from the assorted groups present in the initial emulsion by fractional centrifuging. These were then placed in small cells kept at constant temperatures by water baths and placed on the stage of the microscope. Since the depth of focus of a microscope is very sharp, the number of particles in the field F of the microscope and of a

depth dh could be easily counted. By raising or lowering the microscope, the numbers n at different levels in the volume Fdh could be counted at different depths. The value of h for different settings of the microscope yielding a number n could be read accurately from the graduated head of the adjusting screws of the microscope governing its distance from the solution. Thus n_o, n, and h starting at some arbitrary depth in the solution could be determined. The counting of moving particles in the field was difficult, due to the motions. This was overcome by reducing the field so that about 10 particles appeared at one time. Perrin then counted the number in the field (the bursts of 0 to 10 particles) at various successive intervals of time. By averaging a large number of counts and knowing the area of the field of the diaphragm, he was able to arrive at a fairly accurate value of n.

The most serious difficulty in the measurements lay in an evaluation of m or V, and D. D was determined in three ways: (1) by the use of the pycnometer; (2) by direct measurement of the density of the fused dry gum; (3) by adding KBr, or a salt of known composition, to the solution to increase the density of the liquid until the density of the suspending liquid was so near that of the particles that violent centrifuging would not separate the particles.

1. The pycnometer method consisted in filling the same pycnometer first with distilled water, and then with the suspension at the same temperature, and weighing it. The emulsion was next evaporated to dryness and the resin desiccated at 110°C. and weighed. The dry weight gave the mass of the gum particles present. The difference in the weight of liquid and distilled water gave the excess in mass of all the particles in the suspension over the water which they displace.

2. Unless the process of suspension changes the density of the gum, the density of the dried extracted gum should be the same as that of the particles.

3. The separation of particles by centrifuging, that is, by using powerful centrifugal forces, depends on the fact that the particles or substance of greater density will be thrown outward relatively more than the less dense substance (*i.e.*, the substance of less inertia, the solution). If the densities are the same, separation should be impossible. The precision of this method depends on the centrifugal forces being great enough to separate

particles of small enough differences in density to a noticeable extent in the time intervals used. It also demands that the salt added does not affect the nature of the suspension by causing agglomeration or change of constitution.

The results of the measurements by the three methods on the same suspension for one case are given by Perrin as $D_1 = 1.1942$, $D_2 = 1.194$, $D_3 = 1.195$.

The next problem was the accurate determination of m or V for the particles. The particles appeared as spheres, but the edges were not sharply defined, owing to the diffraction effects. Thus it was impossible to measure the diameter of any one accurately. It happens that if a very dilute suspension be evaporated on an uncovered microscope object glass the capillary forces of the liquid cause the particles to run together in groups. These groups are, in general, one particle in depth and may lie more or less in horizontal rows, or in sheets. Thus the diameter can be found by counting the number in a given area or the number lying side by side in a given straight row. As an example, Perrin found the diameter to be 0.746×10^{-3} mm for the average of 50 rows of from six to seven particles, and 0.738×10^{-3} mm for 2000 particles distributed over 10^{-5} cm^2. Thus if the diameter is known, V can be computed, assuming the particles spherical, and m can be found from D and V. Another way in which the mass of the grains can be found is by direct weighing. In slightly acid solution ($\frac{1}{100}$ normal), while the grains do not adhere to each other, they all adhere to the walls on striking them. Hence, after some hours all the particles are precipitated on the glass walls of the vessel. Thus, by precipitating the grains in this fashion on the walls of small cylinders whose volume could be measured, and by counting the number of grains so precipitated at various parts of the cylinder, a close estimate of the number of grains in the whole small volume of solution was obtained. By then evaporating a known volume of solution, the weight of the particles present could be determined. Thus by dividing the weight so obtained by the number of particles in this volume, deduced by the counting, the mass m of a single particle was determined. A third method of determining the radius of the particles made use of Stokes' law. Stokes has shown mathematically that for spheres moving through a viscous liquid under the action of uniform force, when the spheres are small compared to the diameter of the vessel but large compared

to the discrete structure of the liquid,* the velocity of fall is given by

$$v = \frac{V(D - d)g}{6\pi\eta a} = \frac{\frac{4}{3}\pi a^3(D - d)g}{6\pi\eta a},$$

where a is the radius of the sphere, v the velocity of fall, and η the coefficient of viscosity. This law holds for macroscopic spheres and for microscopic spheres, *if they are not too small.* If v, the velocity of fall of a cloud of suspended particles down a capillary tube, be observed in a liquid (distilled water) for which η is known, a can at once be found. Using these three methods, Perrin found the following values for a from a single emulsion.

	Alignment	Weight	Stokes' Law
a.......	0.371×10^{-4} cm	0.3667×10^{-4} cm	0.3675×10^{-4} cm

With these data then, it was possible to get N_A, for $\frac{n}{n_o}$ and h were observed, while m, or V, D, and d were measured and R_A and T were known.

Before computing N_A, however, it was essential to know whether the equation between $\frac{n}{n_o}$, h, m, and T was verified. This was found to be the case. The results obtained by Perrin in two typical experiments are as follows:

1. Particles of radius 0.212×10^{-4} cm, with 13,000 particles counted at depths of 5×10^{-4}, 35×10^{-4}, 65×10^{-4}, and 95×10^{-4} cm gave $\frac{n}{n_o}$ proportional to 100, 47, 22.6, and 12. Had these accurately followed the exponential law, they would have given 100, 48, 23, and 11.1.

2. In another series of experiments the particles were photographed in a plane normal to the earth's gravitational field and the numbers of particles at various levels were counted on the photograph. These particles had radii 0.52×10^{-4} cm and the distance between the levels was 6×10^{-4} cm. The numbers found for four levels were 1880, 940, 530, and 305. The exponential law leads one to expect 1880, 995, 528, and 280. The deviations are all within the limits of probable variation for the numbers counted. Counts were made on suspensions of differ-

* This assumption demands conditions which are the reverse of those for which the Brownian motions become noticeable. It is to this circumstance that part of the discrepancy between Millikan's result and that of Perrin is ascribed.

ent sorts, η varying in a ratio of 1 to 125. T was varied from -9 to $+60°C.$, while the volume V varied in the ratio of 1 to 50. These suspensions all obeyed the exponential law and led to values for the constant term which yielded a value of N_A lying between 6.5×10^{23} and 7.2×10^{23}. In these values there was no systematic variation of N_A with any factor. It can be safely assumed that the constancy of N_A and the verification of the exponential ratio confirm the assumptions involved in the deduction of the equation beyond a reasonable doubt.

88. The Displacement of the Particles in a Given Time and the Verification of the Brownian-movement Law of Einstein and von Smoluchowski.—The most striking proof of the molecular origin of the Brownian movements lies in the quantitative agreement of the displacements measured in a given time with the predicted value of the displacement based on the theory of Einstein[6] and von Smoluchowski.[7] As was stated, the particles are acted on each instant by unbalanced forces due to unequal molecular bombardment on various sides. The force opposing this motion is the viscous drag of the liquid. As a result of this, the particles move hither and thither through the liquid. If one particle be observed in the field of the microscope which has a series of lines cutting each other at right angles in its field of view, one can plot the position of the particle at any instant on a system of Cartesian coordinates. If the distances of these lines from each other be known, the position of the particle at the end of equal time intervals (*e.g.*, every 30 sec.) can be plotted, and hence the distance it has moved in these time intervals may be determined. Thus the average distance $\overline{\Delta}$ moved through in a given time τ can then be found. This distance depends on the forces acting on the particle, the viscous drag of the liquid, the size of the particle, and other constant factors. If the variation of $\overline{\Delta}$ with η, V, etc. predicted by theory, and the values of the constants computed from observed values of $\frac{\overline{\Delta}}{\tau}$ for a given particle, agree with values obtained in other ways, the underlying assumptions can be taken as completely verified.

The theory for this effect was first deduced by von Smoluchowski and Einstein independently about 1905, and the deduction here given is a simplified treatment due to Langevin.[8] For simplicity, it will be convenient to use not the average displacement of the particle $\overline{\Delta}$ for any time interval τ, but only the x component of

this along one of the observing axes arbitrarily chosen as the x-axis.

Assume that the particle encounters an unbalanced force X along the x-axis. It is retarded in its motion by the viscous drag which for a spherical particle is given by the constant factor in the Stokes' law equation mentioned before. This is

$$f = -6\pi\eta av = -Kv = -K\frac{dx}{dt},$$

where v is the velocity, a the radius, and η the coefficient of viscosity. The equation of motion is, then,

$$m\frac{d^2x}{dt^2} = -K\frac{dx}{dt} + X.$$

Now x may be positive or negative along the axis, for the particle will move in one sense or the other. To get rid of the + and − signs in the equation which occur because the particle moves one way or the other; that is, to enable one to deal with the magnitude of the displacement only, it is easier to modify the equation so as to get rid of x terms and deal only with terms in x^2. To do this, one multiplies by x

$$mx\frac{d^2x}{dt^2} = -Kx\frac{dx}{dt} + Xx.$$

Now

$$x\frac{d^2x}{dt^2} = \frac{1}{2}\frac{d^2x^2}{dt^2} - \left(\frac{dx}{dt}\right)^2$$

and

$$x\frac{dx}{dt} = \frac{1}{2}\frac{d(x^2)}{dt}.$$

Hence,

$$\frac{m}{2}\frac{d^2x^2}{dt^2} - m\left(\frac{dx}{dt}\right)^2 = \frac{-K}{2}\frac{d(x^2)}{dt} + Xx.$$

For a large number of displacements the xX term will, in general, cancel out, for the sign of the xX is as often positive as negative, that is, the average motion is as much in one sense as another. Thus $\overline{Xx}$, the average Xx, is zero. Also, approximately, $pV_A = R_AT = \frac{1}{3}N_AmC^2$, where V_A is the volume of a gram-molecule, R_A is the gas constant for this mass of gas, and N_A is the number of molecules in this volume. Hence the kinetic energy is $\frac{mC^2}{2} = \frac{3}{2}\frac{R_AT}{N_A}$. In dealing with the kinetic energy along the x-axis only,

the kinetic energy along x is $\frac{1}{3}$ the total kinetic energy (see Chap. IX); that is, $\frac{1}{3}\left(\frac{3}{2}\frac{R_A T}{N_A}\right)$ or $\frac{1}{2}\frac{R_A T}{N_A}$. Accordingly, one may set $\frac{1}{2}m\left(\frac{dx}{dt}\right)^2 = \frac{1}{2}\frac{R_A T}{N_A}$. The equation for the displacement as deduced above then loses the Xx term and becomes

$$\frac{m}{2}\frac{d^2\bar{x}^2}{dt^2} - \frac{R_A T}{N_A} = -\frac{K}{2}\frac{d\bar{x}^2}{dt} + 0.$$

Call

$$\frac{d\bar{x}^2}{dt} = z$$

and the result is:

$$\frac{m}{2}\frac{dz}{dt} = \frac{R_A T}{N_A} - \frac{K}{2}z,$$

or

$$\frac{dz}{z - \frac{2R_A T}{N_A K}} = \frac{-K}{m}dt.$$

Integrating this for z from 0 to z, and for t from 0 to t the result obtained is:

$$\left[\log\left(-\frac{2R_A T}{N_A K} + z\right)\right]_0^z = \left(-\frac{K}{m}t\right)_0^t,$$

$$\log\left(-\frac{2R_A T}{N_A K} + z\right) - \log\left(-\frac{2R_A T}{N_A K}\right) = -\frac{K}{m}t$$

$$z - \frac{2R_A T}{N_A K} = +\frac{2R_A T e^{-\frac{Kt}{m}}}{N_A K}$$

$$z = \frac{2R_A T}{N_A K}\left(1 + e^{-\frac{K}{m}t}\right).$$

Now for finite intervals of t of the order of 10^{-5} or 10^{-6} sec. the $e^{-\frac{K}{m}t}$ vanishes. For $K = 6\pi\eta a$ and $m = \frac{4}{3}\pi a^3$, where a is about 10^{-4} cm and η is 0.01 the exponential has the value $e^{-10^9 t}$. If t is greater than 10^{-7}, the quantity $e^{-10^9 t}$ is negligible. Thus restricting the value of t to finite intervals τ of the order of 10^{-7} sec. or more, the quantity $d\bar{x}^2$ must be replaced by $\Delta\bar{x}^2$ and the dt by a finite interval τ in $z\frac{d\bar{x}^2}{zdt}$ and the $e^{-\frac{K}{m}t}$ vanishes. Therefore

$$\frac{\Delta\bar{x}^2}{\tau} = \frac{2R_A T}{N_A K}.$$

Accordingly,

$$\Delta\bar{x}^2 = \frac{2R_A T}{N_A} \frac{\tau}{6\pi\eta a}.$$

Thus $\Delta\bar{x}^2$, the average squared displacement of a particle due to Brownian movements along the x-axis in a time τ, is given by an equation containing the absolute temperature, the gas constant R_A, the Avogadro number, the coefficient of viscosity, and the radius of the particle. It is, consequently, open to simple experimental verification, since all these quantities may be measured, or it can be verified by seeing if $\Delta\bar{x}^2$ varies as predicted, and if N_A fits values from other data. Finally, a verification of the random

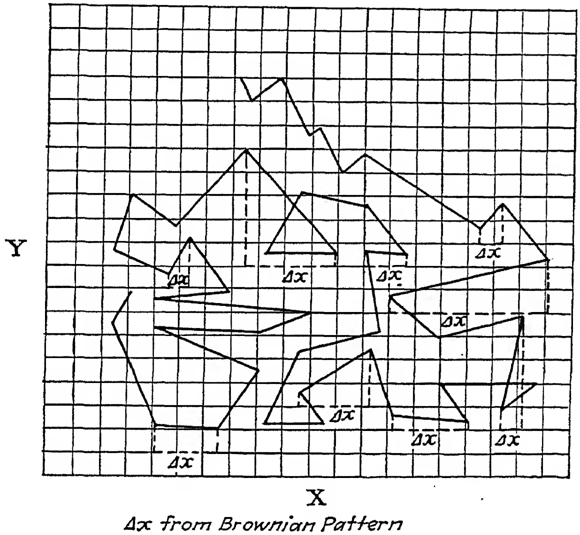

FIG. 50.

nature of the Brownian movements and the verification of the predicted law of diffusion of particles under Brownian movements deduced by Einstein give additional proof.

Perrin made these measurements using the camera lucida and a coordinate system where 16 divisions represented 5.0×10^{-3} cm. The time interval chosen was 30 sec. The average squared x component of these displacements (see Fig. 50) gives $\Delta\bar{x}^2$, and this leads to a test of the theory.

1. *Proof of the Random Nature of the Brownian Motions.*—The distribution of the x projections for a given time was found to be according to the Gauss-Laplacian law of probability which

would be expected as a result of molecular motions obeying Maxwell's distribution law, that is, out of N projections considered, $N \int_{x_1}^{x_2} \frac{1}{\sqrt{2\pi}} \frac{1}{\bar{x}} e^{-\frac{x^2}{\bar{x}^2}} dx$ should have projections lying between x_1 and x_2, the mean square $\bar{x}^2$ being measured as above. Using an emulsion of gamboge with $a = 0.211 \times 10^{-4}$ cm, the number N of displacements lying between successive multiples of the length $x_2 - x_1 = 1.7 \times 10^{-4}$ cm were as follows:

x_1 x_2	One series		Another series	
	N obs.	N calc.	N obs.	N calc.
0 and 1.7	38	48	48	44
1.7 and 3.4	44	43	38	40
3.4 and 5.1	33	40	36	35
5.1 and 6.8	33	30	29	28
6.8 and 8.5	35	23	16	21
8.5 and 10.2	11	16	15	15
10.2 and 11.9	14	11	8	10
11.9 and 13.6	6	6	7	5
13.6 and 15.3	5	4	4	4
15.3 and 17.0	2	2	4	2

This analysis and a series of others on the same subject but using different methods of representation established the completely random nature of the displacements on a quantitative basis.

2. $\overline{\Delta x^2}$ should be proportional to τ. Perrin found that, making τ 120 sec., $\overline{\Delta x^2}$ was about four times what it was for 30 sec., that is, that

$$\frac{\overline{\Delta x_{30}^2}}{\overline{\Delta x_{120}^2}} = \frac{30}{120} = \frac{1}{4}.$$

3. *The Test of the Brownian-movement Equation.*—Up to 1908, tests of the Einstein-von Smoluchowski conclusions were made using the meager data available. They yielded better than an agreement in order of magnitude.

A. The Variation with Temperature.—From the theory above, the average displacements $\sqrt{\overline{\Delta x_1^2}}$ and $\sqrt{\overline{\Delta x_2^2}}$ at two temperatures T_1 and T_2 at which the viscosities are η_1 and η_2 should be in the ratio

$$\sqrt{\frac{\overline{\Delta x_1^2}}{\overline{\Delta x_2^2}}} = \sqrt{\frac{T_1 \eta_2}{T_2 \eta_1}}.$$

For a temperature interval from 17 to 90°C. in one suspension, the variation should have been 2.05 for $\sqrt{\frac{\overline{\Delta x_2^2}}{\overline{\Delta x_1^2}}}$. The observed value was 2.2, which lay within the limits of experimental error for these results.

B. The Variation with η and a, and the Evaluation of N_A.—If the theory is correct, N_A should be given by $N_A = \frac{R_A T}{\overline{\Delta x^2}} \frac{\tau}{3\pi\eta a}$. If a is measured as in the law of atmospheres, then N_A will be determined. The summary of a series of results is given in the accompanying table:

100η	Emulsion	Radius $\times 10^4$ cm	Mass $\times 10^{15}$	Number of displacements	$\frac{N_A}{10^{23}}$
1	Gamboge..............	0.5	600	100	8.0
1	Gamboge..............	0.212	48	900	6.95
4–5	Gamboge in 35 per cent sugar solution.........	0.212	48	400	5.5
1	Mastic................	0.52	650	1,000	7.25
1.2	Large mastic in 27 per cent urea solution.....	5.5	750,000	100	7.8
125	Gamboge in glycerine with 10 per cent water	0.385	290	100	6.4
1	Gamboge of very uniform quality..........	0.367	246	1,500	6.88

Thus masses varying in the ratio of 1 to 15,000 and viscosities varying from 1 to 125 gave sensibly the same value for N_A within the limits of experimental error, so that the equation is verified as regards variation of $\overline{\Delta x^2}$ with these factors. The value of N_A from the last measurements, namely, 6.88×10^{23}, lies within 1 per cent of the value found from the law of atmospheres for the best case, and is near the value 6.2×10^{23} found from L and Van der Waals' b. He therefore adopted the value 6.85×10^{23} as the true N_A. Rutherford, from measurements of the charge for α particles in about 1908, found N_A from e and the Faraday constant to be 6.22×10^{23}, and Millikan's accepted value, based on a measurement of e and a knowledge of $N_A e$, gives $N_A = 6.06 \times 10^{23}$. The proof of the nature of the Brownian movements of Perrin seems, therefore, to be quite conclusive and it may safely

be assumed that these experiments establish the validity of the kinetic theory.

4. *The Application of the Einstein Theory of Rotational Brownian Movements.*—Applying the analysis of Einstein[6] for the rotational movement of Brownian particles, which involves the assumption of the law of equipartition, Perrin was again able to obtain a value of $N_A = 6.5 \times 10^{23}$ which is in good agreement with his translational experiments. This verification therefore also establishes the validity of the equipartition hypothesis as applied to the distribution of rotational and translational kinetic energy.

5. *The Study of the Diffusion Rate of the Brownian Particles and Another Determination of N_A.*—A still further value of N_A was obtained from the diffusion rate of mastic particles in glycerine solutions by Brillouin[9] under Perrin's direction. Einstein predicted that the coefficient of diffusion D should be given by the relation

$$D = \frac{R_A T}{N_A} \frac{1}{6\pi\eta a}$$

for solutions where the particles were so large that the Stokes' law relation held. By measuring D in an ingenious manner, Brillouin was able to evaluate N_A, and found it to be 6.9×10^{23}; in agreement with the earlier work of Perrin on displacements. The absolute values of Perrin for N_A, while consistent with themselves, are, as a whole, higher than those from Van der Waals' b, and from Rutherford or Millikan's values. This difference does not lie in any fault of the theory. It lies chiefly in the inaccuracies present in the difficult measurements of Perrin, notably on the value of a. Another error of some significance in these results lies in the assumptions of Stokes' law as Millikan[3] has shown. As the error was the same throughout, it makes the results of Perrin consistent. Where it was eliminated Millikan was able to get an accurate verification.

89. Accurate Verification of the Brownian-movement Relations for Gases. Millikan's Oil-drop Measurements.—In all Perrin's work the accuracy of the results was limited by the difficulty of evaluating a, the radius of the particles, and also in the Brownian displacement measurements by the uncertainty of the validity of Stokes' law assumed for the small particles used. Furthermore, the results are based on analogy between colloidal suspensions and particles in a gas acted on by molecular impacts.

They are thus open to some theoretical criticism as a complete proof. Millikan overcame this objection in a very striking manner. He worked with minute droplets of oil floating in air or H_2. These took on a spherical form, owing to cohesive forces. He eliminated at one stroke both the assumption of correctness of Stokes' law and the uncertainty in the determination of a by a technique used in the determination of the elementary charge e. To accomplish this, he charged the drop electrically and studied first the lateral Brownian displacements of the drop when suspended in the air, then its rate of fall under gravity alone, and finally under gravity which was opposed by an electrical field acting on the charged drop. The measurements were carried out by Millikan and Fletcher in 1911. As was shown in Sec. 88, a particle undergoing Brownian movement is assumed to be retarded by a viscous force $F = -Kv$. If the Stokes' law holds, $K = 6\pi\eta a$. If it is possible that it does not hold, the use of an undetermined factor K is more accurate for the discussion. Now it is this constant K which depends on a, and, as the law may not hold, the indeterminate form will be used. Assume the particle for which the Einstein equation holds in the form

$$\overline{\Delta x^2} = \frac{2R_AT}{N_A}\frac{\tau}{K},$$

to be placed in a uniform electrical field of strength F parallel to the earth's field. Assume that it has an electrical charge $e\nu$ on it (where e is the electron and ν is some whole number), of such a sign that the force acting on the particle opposes the action of gravity. The drop will then fall under the force mg of gravity with a velocity v_1 if the field is absent. If the field F acts on the drop, it will fall with a retarded speed v_2 under the force $mg - Fe\nu$. Since the retarding force is the same in both cases and the fall is uniform, then

$$\frac{v_1}{v_2} = \frac{mg}{Fe\nu - mg} \quad \text{or} \quad \frac{Fe\nu}{mg} = \frac{v_2 + v_1}{v_1}$$

$$\nu e = \frac{mg}{Fv_1}(v_2 + v_1).$$

Now Stokes' law says that $mg = Kv_1$, so that $\dfrac{mg}{v_1} = K$. Therefore $\nu e = \dfrac{K}{F}(v_2 + v_1)$. For ν equal to unity, $e = \dfrac{K}{F}$ $(v_2 + v_1)_0$ and $K = \dfrac{eF}{(v_1 + v_2)_0}$.

Now Millikan in a separate series had actually determined e, so that it was easy to get ν and to find the value for $\nu = 1$. Actually, e need not have been known, for $e = \frac{K}{F}(v_2 + v_1)_0$ could be found by charging the drop a number of times to different values, and finding the least common divisor for $\frac{K}{F}(v_2 + v_1)$. This would give $\frac{K}{F}(v_1 + v_2)_0$. Thus one could obtain K by observation from v_1, v_2 and F and e.

Putting the value for K into the Brownian-movement equation above, then at once

$$\overline{\Delta x^2} = \frac{2R_AT}{F}\frac{(v_1 + v_2)_0}{N_Ae}\tau$$

or

$$N_Ae = \frac{2R_AT}{F}\frac{(v_1 + v_2)_0}{\overline{\Delta x^2}}\tau.$$

If, accordingly, the Brownian-movement theory is correct, measurements of $\overline{\Delta x^2}$ and $(v_1 + v_2)_0$ for a given τ, T, and F should yield N_Ae, the Faraday constant for the electrolysis of a univalent ion. In these experiments Millikan and Fletcher first held a drop suspended between the plates and measured its Brownian motion along a line normal to the direction of sight and gravity, timing the transits of the drop across cross-hairs of known distance in the eyepiece of the telescope. By using gases of low η and working at lower pressures, values of $\overline{\Delta x^2}$ could be worked with 50 times as large as those of Perrin for the same drop. Hence much more accurate measurements were possible. Next the drop was allowed to fall in the absence of F, and v_1 was determined. Then it was charged to varying amounts and v_2 was measured. From these measurements $(v_1 + v_2)_0$ was determined for a given F. The measurements as made gave the average Δx for a given τ. For convenience, $\overline{\Delta x}$, the average, was computed and then squared. This gave $(\overline{\Delta x})^2$. In the Brownian-movement equation the average of the squares $\overline{\Delta x^2}$ occurs. Thus, to insert the values for $\overline{\Delta x}$ observed into the equation above, it is necessary to employ the relation $\overline{\Delta x} = \sqrt{\frac{2}{\pi}\overline{\Delta x^2}}$, whence $N_Ae = \frac{4}{\pi}\frac{R_AT}{F}\frac{(v_1 + v_2)_0}{(\overline{\Delta x})^2}$.

The temperature in these measurements was also easily more accurately controlled by a thermostat than in those of Perrin. The results should, consequently, be more reliable. With 1735 displacements on a drop with unit charge, Millikan and Fletcher got $N_A e = 2.88 \times 10^{14}$ electrostatic units. For a univalent ion in electrolysis, $N_A e$ comes out as 2.89×10^{14} electrostatic units. The probable error on the number of counts used is 2 per cent and the observed difference is well within this limit. Both in the accuracy of the result and in the avoidance of any questionable assumptions this beautiful piece of work confirms Perrin's conclusions in a striking manner, and can be regarded as one of the triumphs of modern technique in experimental kinetic theory. It definitely establishes the correctness of the kinetic-theory explanation of Brownian movements and thus verifies the kinetic theory of matter beyond a doubt.

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Books Recommended

a. Perrin, J.: *Loc. cit.* A classic that every physicist and chemist should read.

b. Millikan, R. A.: *Loc. cit.* Another classic of modern science.

c. Bloch, E.: "Kinetic Theory of Gases," Chap. VII. Methuen, London, 1924. An excellent summary of modern kinetic theory for more popular consumption.

CHAPTER IX

SPECIFIC HEATS AND THE KINETIC THEORY

90. Definition of Specific Heats and the Simple Experimental Facts.—After the perfection of thermometry to a point where physicists could discuss such measurements from a common viewpoint, the next great advance made in the field of heat was the definition of a term which is called the quantity of heat. In the master mind of Black,[1] the obvious interpretation of his measurements connoted to him the existence of an imponderable heat fluid which he could measure. The heat theory based on this connotation is, of course, now completely abandoned, as a result of the interpretation of heat in terms of the kinetic theory which arose scarcely 60 years later. It still remains to interpret this very definite concept, the quantity of heat, in terms of a theory ascribing all heat to the kinetics of gas molecules. Closely associated with the concept of heat quantity is another concept inseparable from it, and without which the definition of a unit of heat quantity is impossible. This quantity is defined as the specific heat. It is the capacity of a body to absorb heat for a given rise in temperature. The unit commonly used in physics is a purely arbitrary one, based for convenience on the most serviceable and common substance used in heat-quantity measurements, to wit, water. The definition of the precise unit is at present much a matter of choice, the convenient unit used being easily convertible into any other unit. This situation arises from the fact that the specific heat of water, *i.e.*, its thermal capacity, varies with the temperature. It is, in general, defined as the heat required to raise 1 gram of water 1°C. at a given temperature which is convenient for the work in hand. Since the change of heat capacity of water with temperature is known, all these may be referred back to the heat necessary to raise 1 gram of water 1°C. at 20°C. This unit of heat quantity is called the gram-calorie. It furnishes a convenient reproducible unit in which to define heat quantity. If with this unit the heat required to raise a gram of any other substance 1°C. be measured, the heat

capacity of that substance relative to water is obtained, or its *specific heat.* This is measured and expressed in terms of calories. A table of values of the specific heats of a number of common substances is given below in order to represent the order of magnitude of the quantities involved.

Substance	Temperature, degrees centigrade	Specific heat at constant pressure	Temperature, degrees centigrade	Specific heat at constant volume
Water	0	1.0094		
Water	20	1.0000		
Mercury	20	0.0333		
Silver	15–100	0.0560		
Aluminum	15–185	0.2190		
Lead	20–100	0.03050		
Carbon (graphite)	11	0.160		
Benzene	10	0.340		
Ice	21– 1	0.502		
Air	20	0.2417	0	0.1715
Hydrogen	......	3.4020	50	2.402
CO_2	0	0.2010	55	0.1650
Argon	20– 90	0.123	0–200	0.0746
Water vapor	100	0.4652	100	0.340

It is to be noticed that there are in the table two types of specific heats listed—those taken at constant pressure, and those taken at constant volume for gases. The former, designated in what follows by the symbol C_p, is the amount of heat required to raise the temperature 1°C. when the substance is expanding against a constant pressure. Thus this quantity is the heat required to raise the temperature plus that which goes into the work of expanding against the atmospheric pressure. For solids and liquids this is small, and C_p nearly equals the other specific heat, that at constant volume, designated hereafter by C_v. C_v is the heat required to raise 1 gram of the substance 1°C. when the volume is constant, that is, when it does no work. In this sense it measures the true heat capacity of the substance. For gases where expansion is appreciable, C_p contains an appreciable heat expenditure as external work and is distinctly greater than C_v. For solids this is less but is not negligible, as was shown by G. N. Lewis[2] for a number of pure substances.

It is also seen in the table that this quantity varies from 3.4 for hydrogen down to 0.033 for some solids, water having the next highest specific heat to hydrogen. Furthermore, there is, apparently, no regularity in the way in which they vary except that the lighter elements or substances seem to have the highest specific heats. For substances whose densities change rapidly with temperature there is, in general, a rapid change of specific heat with temperature. Thus it might be suspected that, by some correlation of weight or density, the apparent disorder of the values of the specific heats could be changed to show more regularities. In investigating the specific heats of pure elements two Frenchmen, Du Long and Petit, in 1819 observed the important fact that for most solid elements the specific heat multiplied by the atomic weight was a constant, and took on a value of about 6 cal.

TABLE OF ATOMIC HEATS

Substance	Atomic weight	Specific heat	Product
Al	27.1	0.2143	5.80
Pb	206.4	0.0314	6.48
Br	79.76	0.0843	6.33
Fe	55.9	0.1138	6.36
Au	196.7	0.0324	6.37
Cu	63.18	0.0952	6.01
K	39.03	0.1655	6.46
Li	7.01	0.9408	6.59
P	30.96	0.1895	5.87
Hg (solid)	199.8	0.0319	6.37
S	31.98	0.1776	5.68
Ag	107.66	0.0570	6.14
Bi	208.38	0.0308	6.42
C (diamond 10°C.)	11.97	0.1128	1.35
C (diamond 985°C.)	11.97	0.4589	5.49
C (graphite 10.8°C.)	11.97	0.1604	1.92
C (graphite 985°C.)	11.97	0.4674	5.60
B (26°C.)	10.9	0.2382	2.60
B (233°C.)	10.9	0.3663	3.99
B (red heat)	10.9	0.50	5.45
Si (crystalline, 21.6°C.)	28.3	0.1697	4.80
Si (crystalline, 232.4°C.)	28.3	0.2029	5.74

Since a gram-molecule or a gram-atom of a substance is its molecular or atomic weight in grams, this law says that for such simple substances it takes 6 cal. to raise a gram-atom 1°C. Now this at once suggests an interesting conclusion, for by Avogadro's rule (see Sec. 8), the gram-atom of all substances has the same number of atoms. Hence for these elementary solid substances it takes the same amount of heat to raise the atoms in a gram-atom of the solid 1°C., irrespective of the substance. This rule holds well (if the C_p measured is converted to C_v) at ordinary temperatures for all but boron, carbon, and silicon, where the atomic heats are much lower. Investigation shows that these increase their atomic heats, approaching 6 as the temperature is

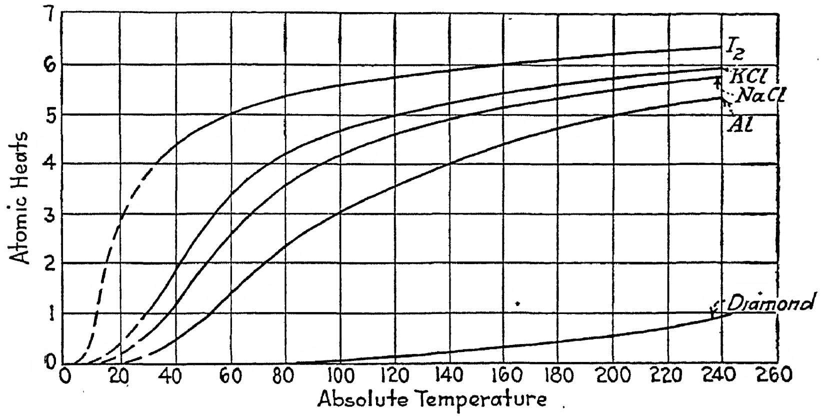

FIG. 51.

raised, while the others all fall below 6 cal. as the temperature falls. At absolute[19] 0 all atomic heats approach 0, as shown by the curves of Fig. 51. At very high temperatures the atomic heat for elements normal at room temperatures begins to increase slowly above the value 6.

If the same criterion be applied to the values of C_p and C_v for gases, the apparent chaos disappears and again a semblance of order appears, with, of course, some deviations. The atomic or molecular weight of the gas multiplied by C_v and C_p gives the following approximate values for three types of gases:

	MC_v, Calories	MC_p, Calories
Monatomic gases	3	5
Diatomic gases	5	7
Polyatomic gases	6	8

In the diatomic gases certain chemically very reactive gases, such as Cl_2 and Br_2, show distinctly higher values than the rule permits. This holds true also for many of the polyatomic gases, particularly those regarded as chemically reactive at ordinary temperatures. At higher temperatures these approximate constants *all* increase in value, while those deviating at room temperatures tend to conform to the rule as the temperature decreases. Finally, the general rule may be applied to a number of compounds of definite molecular composition. Neumann[35] found that for oxides and sulphides of the form indicated below the molecular heats took on values characteristic of the molecular constitution.

Type of Oxide	Molecular Heat	
RO	11	$= 5.5 \times 2$
RO_2	14.0	$= 4.7 \times 3$
RO_3	18.4	$= 4.6 \times 4$
R_2O_3	26.9	$= 5.4 \times 5$
RS	11.9	$= 5.9 \times 2$
RS_2	18.1	$= 6.0 \times 3$
RCl	12.75	$= 6.4 \times 2$
RCl_2	18.7	$= 6.2 \times 3$
RNO_3	24	$= 4.8 \times 5$
$R(NO_3)_2$	38.2	$= 4.2 \times 9$
RSO_4	26.4	$= 4.4 \times 6$
R_2SO_4	32.9	$= 4.7 \times 7$
RCO_3	21.4	$= 4.3 \times 5$
R_2CO_3	29.1	$= 4.9 \times 6$

Thus there is, clearly, a heat contribution which is roughly proportional to the number of atoms in the molecule, which is, however, influenced in magnitude by certain constitutional differences for specific types of groupings. This remarkable discovery of Du Long and Petit was not only of great use to the chemist in his attempts to establish the correct formulæ for his compounds, but lead to an expression for the specific heats which put them into some semblance of order. This order remained unexplained for many years and the kinetic theory offered the first and only explanation. The clue to the meaning of these laws is suggested by the rule of Avogadro that points to the fact that, in elementary solids, the same number of atoms under certain conditions have the same specific heat. Not only have the regularities proved of use, but the very irregularities or deviations have yielded a remarkable service in showing where the classical treatment and understanding ended and the mysterious quantum actions began. In fact, the applications and limitations

of the treatment of specific heats by the kinetic theory furnish one of the most dramatic and fascinating chapters of the kinetic theory and perhaps one of its strongest supports.

91. The Doctrine of Equipartition of Energy and the Distribution of the Energy among the Degrees of Freedom there. *A. Review of Assumptions Involving Equipartition of Energy.*—In Sec. 9 it was shown that if the interpretation of pressure by the kinetic theory is accepted and is combined with Avogadro's rule, for point molecules, making elastic impacts, it follows that, on the average, every type of molecule of a gaseous mixture has the same kinetic energy, and this energy is related to the temperature of the gas. Thus, if two types of molecules m_1 and m_2 of average velocities C_1 and C_2 existed in a gas of pressure p in a volume v at a temperature T, then

$$pv = \frac{1}{3} n m_1 C_1^2 = \frac{1}{3} n m_2 C_2^2 = RT,$$

where n is the number of molecules in each volume. Since by Avogadro's rule $\frac{n}{v}$ is the same for all gases at constant pressure and temperature,

$$\frac{1}{2} m_1 C_1^2 = \frac{1}{2} m_2 C_2^2 = \frac{3}{2} \frac{R}{n} T,$$

where $\frac{R}{n}$ is the value of R appropriate to a single molecule. This means that the kinetic energy of translation of the molecules m_1 and m_2 in a mixture of gases is, on the average, the same, or the kinetic energy is distributed evenly among the molecules, whether of different types or not.

This idea is capable of being pushed further and has been actually carried further in Chaps. II and IV.* There it was assumed that in a gas in equilibrium the velocities were equally distributed along the three coordinate axes—that is to say, that the x, y, and z components of c, or u, v, and w, were, on the average, equal. In this case, then, the energies associated with the velocities u, and w along the axes, which are proportional to u^2, v^2, and w^2,

* A more rigorous proof of the theorem of equipartition of energies as a result of the conditions underlying the Maxwellian distribution of velocities is given in Sec. 36 of Chap. IV.

are also equal. For a gas where the molecules can show only motions of translation along the three axes (*e.g.*, the monatomic gases), the energy is composed of the kinetic-energy components of its motion along the three coordinate axes, and these, on the average, are equal.

B. Definition of Term "Degree of Freedom" and Extension of Idea of Equipartition to Rotation and Vibration.—In discussing motion in what follows, the allowable independent motions which a body can make will be termed its *degrees of freedom of motion.* Thus, for example, a body that can have only motions of translation has only three independent motions possible, *i.e.*, those along the three axes. It is said to have three degrees of freedom of motion. A body which can rotate about three independent axes has, then, besides its three degrees of freedom of translation, likewise three degrees of rotation. Finally, a body composed of two or more molecules bound by elastic forces may have vibratory motions of the molecules along their lines of junction. Each such vibrational mode which is independent of any other constitutes a new degree of freedom of motion. It may be pointed out, in this connection, that for such a motion under elastic restoring forces, on the average, one half the energy is at any instant in a kinetic form, the other half is in the potential form. Thus a body may have, at most, three degrees of translational freedom, three degrees of rotational freedom, and as many degrees of vibrational freedom as there are independent modes of vibration possible, each vibrational mode, however, having equal quantities of kinetic and potential energy. The law of equipartitions of energies may from the foregoing then be stated by the assertion that *the energy of a gas is on the average distributed equally among the degrees of freedom.*

C. Existence of Rotation Proven.—Thus far in the text attention has been focused on the translatory motions of the molecules. That, with the assumption of elastic impacts and equipartition, one should also expect rotational motions in which each degree of freedom has as much energy as each degree of translational freedom cannot be questioned, where molecules with moments of inertia exist. Experimentally, the work of Perrin has shown that the larger particles undergoing Brownian movements do exhibit rotations, and he has proved these to be rotational heat motions, similar to those for molecules, by quantitatively verifying Einstein's equation for this case (see Chap. VIII, Sec. 88). A further

proof of existence of the rotations and vibrations of atoms in molecules comes in a striking fashion from the theory of band spectra. An atom in which an electron is emitting light, as was shown in Sec. 46, has the single line of negligible width broadened as a result of the Doppler principle and the translational motions coupled with the distribution of velocities. If, now, a molecule be considered in which, owing to the moments of inertia of the atoms about their common center of gravity, rotations of the molecule as a whole may be expected, then if one of the atoms be emitting a spectral line, the line will be displaced to the one side or the other of the line emitted by the atom at rest, due to the rotation and the Doppler principle. For rotations as well as translations then the lines would be broadened, owing to the distribution of velocities among the molecules. In rotation, however, there is a mysterious action which restricts the continuity of the distribution of rotational velocities, while it does not do so in translation. For some reason at present unknown, a molecule may rotate about its center of gravity in such a fashion that its kinetic energy of rotation $\frac{1}{2}I\omega^2$ (where I is the moment of inertia and ω is its angular velocity) is only whole multiples of an energy $h\nu$, ν being the frequency of rotation and h being the universal constant of Planck.[3] Thus unlike the translational motions which can take on a large continuous range of values dictated by the Maxwell distribution law around room temperatures, the rotational velocities can take on values of only $h\nu$, $2h\nu$, $3h\nu$, $4h\nu$, etc. Thus one would have, besides the single broadened line due to translation for a light emitting molecule, a pair each of lines displaced one to each side of that line corresponding to the $1h\nu$, $2h\nu$, $3h\nu$, etc. of rotation. In a similar manner, the quantization of the vibrations will superpose more displacements of the single line emitted, in which, due to many different values of ν for vibration, the displacements may be different, so that for each line emitted by an atom of the molecule there will be a group of lines, closely related to it in frequency, constituting a single band or a system of bands. The spectrum of such a molecule will then consist of a system of bands corresponding each one to a single electronic frequency within the atom with the velocities of rotation and vibration so compounded with it that each single line becomes a band or group of bands of definite structure. In some cases these bands are in the infra-red, in others they lie in the visible. For many

gases they have been analyzed and from the distance between the components of a band it has been possible to compute the moments of inertia of the molecule and the distances between atomic centers.[6,4] Similar calculations for the vibrations lead to an evaluation of the law of attraction and the forces between the atoms. The values for these forces are now being checked in a spectacular fashion by Birge[5,6] on the basis of the "swelling" of the atom due to the centrifugal forces of rotation. In fact, the uncanny precision of the explanation of such a multitude of phenomena by the assumptions of *quantized rotations and vibrations* has caused their unqualified adoption in the field of spectroscopy. This is carried so far that whenever a band spectrum is observed it is taken for granted that it represents a molecular compound, even when it occurs in gases where to the chemist's knowledge molecules do not exist (*e.g.*, in such gases as He and Hg and Ar). This evidence may then be accepted without hesitation as proving the existence of rotational motion among molecules, and as further evidence that the distribution of energy among the various rotational states is governed, contrary to the translations, by the restrictions of the quantum theory.

D. Application of Equipartition to Rotation and Vibration and Limitations Imposed by Quantum Theory.—Thus having assumed rotations to exist, and having accepted the doctrine of equipartition of energy for translation, it is not a great step to assume that the principle of equipartition must apply to the gas as a whole, that is, to rotational as well as to translational motion. As far as the quantum theory,* which was perhaps introduced somewhat prematurely in the last paragraph, is concerned, it has no conflict with this assumption. While it restricts the energies which single rotations of a given atom can take on to a limited number of values instead of the infinity to be expected from a continuous distribution law, it does not in any way prevent the particular degree of freedom as a whole from taking its full quota of the energy of the gas. What it does do, however, is to restrict the activity of a given rotational or vibrational degree of freedom in certain cases, as will be seen. In fact, there is an actual experimental case on record where, owing

* It may be added that the term "theory" in "quantum theory" is perhaps a misnomer. It is from *observation* by experiment only that the physicist has been lead to the necessity of adopting the quantum concept in order to correlate the results of observation. The quantum is an observational fact, not a theory.

to the *quantum action, the rotational degrees of freedom of H_2 gas disappear at low temperatures and it acts as a monatomic gas.* The restriction of the quantum theory to the application of the law of equipartition perhaps might be stated as follows: Wherever a degree of freedom can, under the quantum restrictions, assume its full activity, the law of equipartition of energy among the degrees of freedom may be applied without question.

As regards the quantum restrictions in equipartition for vibrational degrees of freedom, the same may be said as for rotation. The extension of the doctrine of equipartition to the vibrations of the atoms is, in general, a little more doubtful. In this case the vibrations are intramolecular. If these vibrations lead to dissipation of the energy in any other form than that of mass motion of the atoms (*e.g.*, in radiation which can escape from the gas or in chemical work of separation, dissociation, of the atoms), the impacts are inelastic. This is an assumption which has been carefully avoided in the kinetic theory and must be so in order to study the gases under sufficiently simple conditions. Thus in including the vibrations in the category of degrees of freedom to which equipartition can be applied, the restriction must be added that this can only be done where the elasticity of impacts is preserved and no changes in the kinetic energy of the gas as a whole take place.

E. Calculation of Cv for Various Types of Gases from Equipartition among Degrees of Freedom.

Returning to the relation that $\frac{1}{2}mC^2 = \frac{3}{2}\,\frac{RT}{n} = \frac{3}{2}\,kT$ (where $\frac{3}{2}kT$ is the energy of translation for one atom), it is seen at once that *each* of the three degrees of freedom of translation, on the average, takes an energy $\frac{1}{3}\left(\frac{3}{2}kT\right)$, or $\frac{1}{2}kT$. Thus the law of equipartition may be stated by saying that to each degree of freedom of a gas molecule the energy associated with it is, on the average, $\frac{1}{2}kT$. Accordingly, for a gram-molecule, since 22,400 $Nk = R_A$, is about 2 cal. for 1°C. (accurately, R = 1.9885 cal.), it can be said that each degree of freedom corresponds to $\frac{2}{2}T$ cal. Hence, if the temperature of a gram-molecule of the gas be raised 1°C., the heat taken to increase the energy of the degree of freedom by an amount corresponding to this is roughly 1 cal. Thus

the molecular heat for each degree of freedom is 1 cal. It is now possible to apply the above assumption to the practical cases exhibited by different types of gases. For a monatomic gas like He, Ar, or Hg, all but $\frac{1}{3720}$ of the mass or even less is concentrated at the center of the atom in a nucleus whose radius is of the order of $\frac{1}{50,000}$ that of the atom.[7,8] Accordingly, the fraction of the energy involved in rotation may be considered negligible.* Such gases can have only three degrees of freedom of translation along the three coordinate axes. The atomic heats of all such gases should be 3 × 1, or 3 cal. Measurement shows this to be the case within the limits of experimental error. In a diatomic gas in which vibrations do not occur, there are two massive points moving as a rigid whole. This system can have its center of gravity moving along the three axes. It may also exhibit rotation of the two masses about two axes at right angles to each other and to the line adjoining the two atoms, that is, it may have three degrees of freedom of translation and two degrees of freedom of rotation, making a total of five degrees of freedom of motion. To each of these is permitted 1 cal. for all the molecules in a gram-molecule. Hence for these MC_v should be 5 cal. This is seen to be the case for most chemically inert gases within

* How the energy of rotation of *atoms* may be neglected on the quantum theory may be seen at once from what follows. According to that theory,

$$E_r = \frac{1}{2} I\omega^2 = \frac{I}{2} (4\overline{\pi\nu^2}) = n\frac{h\nu}{2},$$

where E_r is the energy of rotation that must be quantized, I is the moment of inertia, ω the angular velocity, ν the frequency, h the Planck constant, and n an integer taking successively values (0, 1, 2, 3, 4, 5 . . .).

Hence

$$\nu_n = \frac{nh}{4\pi^2 I}, \quad n = (0, 1, 2, 3, 4 \ . \ . \ .)$$

and

$$(E_r)_n = \frac{n^2h^2}{8\pi^2 I}.$$

If I is very small, E_r is very large and the energy necessary to activate these quantum states is so much above the normal thermal energy that no energy of rotation is absorbed by the atoms of He, Ar, and Hg. This peculiar action of the quantization of energy will be discussed more in detail later in this section. If the radius of the atom is 10^{-8} cm, the electron mass is 9×10^{-28}, $h = 6.5 \times 10^{-27}$ ergs sec., $n = 1$, E_r takes a value of 10^{-11} ergs. This is a thousand times the energy of thermal agitation at 273° absolute. So at room temperatures there is not energy enough in the atoms to cause such a spin of the electrons.

the limits of experimental error. For all other polyatomic gases there are three degrees of freedom of rotation and three of translation. Hence MC_v should be 6. This is the case for a few. With most of them MC_v is greater than 6, and this is the more so the more reactive the gas is chemically. As the temperature is lowered, MC_v for such gases decreases and approaches 6 calories.

All this indicates definitely that for some of the more complicated gases energy is going into other channels than that of increasing the translatory or rotational energies. It can go into only two other channels, that of increasing vibrational energy along the lines of junction of the atoms, an act which might ultimately cause a loss of heat energy to work of dissociation, or that of displacing electrons in the molecules from their positions of equilibrium to new positions of greater energy content. The non-existence of ionization of the gas or light emission at ordinary temperatures definitely rules out the electronic vibrations as the cause for the higher molecular heats of such gases.[13] Furthermore, most molecular gases obey the gas laws either in their elementary form or in the form of Van der Waals' equation, and dissociation does not occur at ordinary temperatures in most gases. It may therefore be concluded that for most polyatomic gases the high molecular heats are due to the activity of degrees of freedom of vibration inside the molecules. These degrees of freedom, however, do not necessarily demand inelasticity of impact in any sense.

F. Brief Statement of Quantum Theory.—If the atom is regarded as a system of electrons in orbits about a central sun or nucleus, and molecules as the grouping of two or more such celestial systems in positions of equilibrium relative to each other, the question arises as to why the impacts should be elastic at all, that is, why at impact could not the kinetic energies be used in semipermanent distortions of the molecules which increase their potential energy and cause dissipation of energy as radiation. It is here that a generalization from other fields, and one which early found its application in specific heats, may be applied. The first to realize the application of quantum theory to specific heats was Einstein[9] in 1907. Work on the radiation laws had lead Planck[10] in 1900 to conclude that these could be derived only on the assumptions that energy was absorbed or emitted in whole units or quanta. These quanta he showed consisted of the frequency of vibration of the oscillator multiplied by a universal constant h. Einstein[11] in 1905 indicated that the

energy of electrons liberated by light from a metal, the photo-electrons, should be $\frac{1}{2}mv^2 = h\nu - P$, where ν was the frequency of the emitting light and P was the work to get an electron out of surface. This law was subsequently proved experimentally by Millikan[12] in 1916. In 1913, experiments by Franck[13] and Hertz had shown that electrons collided elastically with atoms, that is, they retained their energy gained from the field unless the energy exceeded that necessary to ionize the atom. This was later also shown to apply to the process of light emission in that it was found that, to excite radiation of light by the bombardment of atoms by electrons, atoms and electrons were unaffected by impact unless the energy at impact exceeded the value of $h\nu$ characteristic of the light excited. All of these may be correlated as belonging to phenomena which were summed up by Bohr[14,15] in his formulation of the structure of the atom begun in 1913. In this formulation, Bohr postulated that for an electron moving about a nucleus on the inverse-square law of force the electron, although accelerated, does not radiate energy as classical electrodynamics requires; and that, furthermore, it was not possible for the electron to assume *any* orbit consistent with the force and its velocity. He assumed that the electron could take on a limited number of definite orbits, in which it could move without radiation. In order to be disturbed, an electron in such an orbit *had to receive energy enough in the encounter to move it to one of the next outer stable orbits*, that is, it could only be removed from an orbit to an outer one when it received from the impinging electron an energy equal to that of moving it to a higher orbit or out of the atom. Light was emitted then only in the process in which the electron fell back from an outer to an inner orbit and the energy radiated was $h\nu$. The frequency ν of the radiation was connected with the orbital frequency by what is known as the correspondence principle. This group of assumptions has had such a remarkable success in correlating the spectroscopic data that, together with the experimental evidence on inelastic impacts and radiation laws, they must be accepted as essentially in conformity with nature, although the mechanism of the processes remains quite obscure.

G. Effect of Quantum Restrictions as Regards Equipartition of Electronic Vibrational and Rotational Energies.—The important feature of these quantum assumptions for the problem of specific heats lies in the problem dealing with the effectiveness of impacts

in setting rotations or vibrations into action or in disturbing the electronic configuration of the atom. Thus on this basis it would not be expected that an electron in an atom should be excited on impact unless it received energy enough to raise it to a level where in falling back to its original position it would radiate light of a frequency ν. For an electron emitting one of the D lines of yellow sodium light $\nu = 5.095 \times 10^{14}$. Planck's constant h is 6.62×10^{-27} ergs sec., whence $h\nu = 3.37 \times 10^{-12}$ ergs. The average energy of an electron or of a molecule at 0°C. is 5.62×10^{-14} ergs. Thus it would be a rare impact between atoms in which the relative energy imparted to one electron would be 50 times the average energy of agitation. The quantum condition for an inelastic impact would, therefore, be fulfilled but rarely and the majority of the impacts would be elastic. It is therefore to be expected that degrees of freedom of electronic vibration are only to be awakened at temperatures where the average energy of agitation of the molecules or atoms becomes comparable with the quanta required for light emission by electrons. That such processes do occur at high temperatures is evidenced by the emission of spectral lines in flames when the adequate temperatures are reached.[16] At room temperatures, however, practically all impacts are elastic as regards losses to electrons. For the vibrational energies in molecules ν is very much lower, that is, the light radiated is in the infra-red and for rotational energies the frequency is yet still lower. Hence in this region it is not surprising that, since $h\nu$ is not much greater than the 5.62×10^{-14} ergs of energy of agitation, an appreciable fraction of the collisions set the molecules into vibration along the line of centers. Thus MC_v should be expected to show signs of increasing at room temperature. If, on the average, one-half the molecules were kept vibrating with one quantum of energy, then, since equipartition demands that each vibrational degree take 2 cal., it would be expected that the value of C_v would be 7 instead of 6 cal. for a polyatomic gas, and 6 instead of 5 cal. for a diatomic gas. This is the case for Br_2, where MC_v is about 5.82 instead of 5, and less so for Cl_2, where MC_v is 5.2. It is clear that, as the temperatures are raised, gases which had the number of calories for MC_v that theory demanded would begin to increase their molecular heats, and that as the temperatures were lowered gases like Cl_2 and Br would begin to conform to the general rule. This appears to be so experimentally.

Since rotational quanta require still less energy, it is not surprising that at room temperatures the molecules all show their full quanta of rotation. At very low temperatures this should not be so. Unfortunately, all molecular gases other than H_2 liquefy at temperatures so high that a marked decrease in the rotational energy has not set in. In H_2 luckily, it had been shown by Eucken[17] in 1912 that at temperatures below the boiling point of liquid air the molecular heat of the gas rapidly diminishes, reaching a value characteristic of a monatomic gas at about 60° abs. This, as will be seen in what follows, can only mean that at such temperatures the average kinetic energy of thermal agitation is so low that it is only rarely that the molecule has an energy

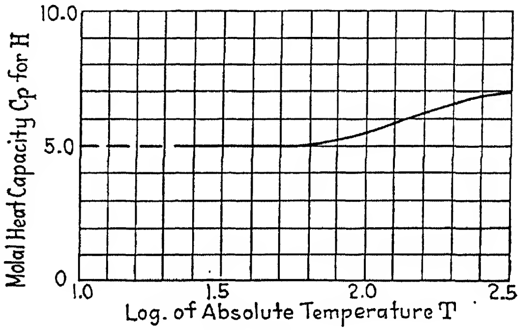

FIG. 52.

imparted to it, equivalent to the $h\nu$, for rotation, and hence capable of imparting rotational degrees of freedom to the gas. This can be seen in Fig. 52, where C_p for H_2 is plotted against the $\log_{10}$.^{T}*

92. The Specific Heat at Constant Pressure C_p, and γ, the Ratio of the Specific Heats, $\frac{C_p}{C_v}$, as Interpreted on the Kinetic Theory.—Consider a gas in a vessel provided with a weightless piston in contact with a heat reservoir. If the gas is insulated for heat losses its temperature will gradually increase due to the heat inflow. As the temperature increases, the gas will expand, driving the piston outward. If the initial pressure was p, the outside atmospheric pressure, the gas in expanding by an amount Δv

* Recent measurements of Cornish,[18] at the University of California, have established the correctness of this with remarkable precision.

will do the external work $p\Delta v$ against the outside pressure p. In addition to this, the kinetic energy of the gas will increase by an amount corresponding to $\frac{R}{2}dT = dT$ cal. for each gram-molecule of gas for each degree of freedom of mechanical motion active. If the gas is one in which degrees of freedom of vibration can exist, then again $\frac{2R}{2}dT$, or $2dT$ cal., will be absorbed by the gram-molecule of the gas per degree of freedom of vibration. Finally, if the intermolecular forces are very great (*e.g.*, Van der Waals' a is appreciable) and dv is great, then some work will be done in increasing the potential energy of the gas. If Δv is small, since a is generally minute, this term may be neglected and $\int_0^{\Delta v}\frac{a}{v^2}dv$ can be set equal to 0. Thus $C_p dT = \Delta(KE)_T + \Delta(KE)_R + \Delta(E)_v + p\Delta v$, where $\Delta(KE)_T$ represents the gain in translatory kinetic energy, $\Delta(KE)_R$ the gain in rotational kinetic energy, $\Delta(E)_v$ the gain in vibratory energy, and finally $p\Delta v$, the external work done against pressure.

Now $pv = RT$ to a first approximation and hence for small volume changes $p\Delta v = RdT$. Thus, expressing the relation for the heat absorbed $C_p dT$, where C_p is the specific heat at constant pressure, in terms of R and dT one has

$$C_p dT = \frac{3}{2}RdT + f_1\frac{1}{2}RdT + f_2 RdT + RdT,$$

where $\frac{3}{2}RdT = \Delta(KE)_T$, $\frac{1}{2}f_1 RdT = \Delta(KE)$, $f_2 RdT = \Delta(E)_v$, $RdT = P\Delta v$, and the factors f_1 and f_2 represent the degrees of freedom of rotation and vibration present. Thus

$$C_p = \left(\frac{5}{2} + \frac{f_1}{2} + f_2\right)R.$$

As $R = 2$ cal., one may write

$$C_p = (5 + f_1 + 2f_2).$$

For a monatomic gas $f_1 = 0$ and $f_2 = 0$. Hence $C_p = 5$ cal. For a diatomic gas $f_1 = 2$ and $C_p = 7$ when $f_2 = 0$, while for a polyatomic gas where $f_2 = 0$, $C_p = 8$. For a gas with $f_1 = 2$, $f_2 = 1$, and for a gas with $f_1 = 3$, $f_2 = 1$, C_p becomes 9 and 10 cal. respectively. These last figures are approximated under certain conditions by gases such as Cl_2 and C_3H_8.

In general, while C_p is known, γ, the ratio of the specific heats, $\gamma = \frac{C_p}{C_v}$, is much more accurately known, for it can be found by direct measurements of C_p and C_v, from the velocity of sound in a gas, and by adiabatic and isothermal expansion methods such, for instance, as the Clement-Des Ormes method.

Using the notation of this section, $C_v dT$ may be given by

$$C_v dT = \Delta(KE)_T + \Delta(KE)_R + \Delta(E)_v,$$

or

$$C_v = \frac{3}{2}R + \frac{1}{2}f_1 R + f_2 R,$$

whence

$$\frac{C_p}{C_v} = \gamma = \frac{3/2 R + 1/2 f_1 R + f_2 R + R}{3/2 R + 1/2 f_1 R + f_2 R}.$$

Thus one has for γ

$$\gamma = \frac{C_p}{C_v} = \frac{(5 + f_1 + 2f_2)}{(3 + f_1 + 2f_2)}.$$

For monatomic, diatomic, and polyatomic gases this gives γ as $5/3 = 1.66$, $7/5 = 1.40$, $8/6 = 1.33$ respectively. Where $f_1 = 2$ and $f_2 = 1$, and also where $f_1 = 3$ and $f_2 = 1$, that is, for diatomic and polyatomic gases with one vibrational degree of freedom, γ is $9/7 = 1.286$ and $10/8 = 1.25$. It is seen that as f_2 increases beyond unity γ will gradually approach 1 as a limit. Below is given a table of the values of γ for a number of gases and it is seen that γ varies as is predicted, reaching values near 1 for such complicated gases as ether vapor where many vibrational modes may be operative. It is possible, however, with ether that the internal energy of expansion may need to be taken into account in order to compute a correct theoretical value for γ. How well these laws are obeyed may be seen from the observed values of γ given below:

Observed γ for Gases

Monatomic Gases		Diatomic Gases		Polyatomic Gases	
He	1.63	Air	1.401	O_3	1.29
Ar	1.667	H_2	1.408	H_2O	1.305
Kr	1.66	O_2	1.400	CO_2	1.300
Hg	1.66	CO	1.401	NH_3	1.336
		NO	1.394	CH_4	1.313
		Br_2	1.293	C_2H_6	1.22
		Cl_2	1.323	C_3H_8	1.130
				Ether	1.024

93. Atomic and Molecular Heats of Solids.—In view of what has gone before in the case of gases, it is a simple matter to explain the law of Du Long and Petit on the kinetic theory. In the solid state, and especially in crystals, it is assumed that the atoms or molecular groups are bound in fixed positions relative to each other. Thus there is not the motion associated with the solid state that characterizes the liquid and gaseous states. Heat motions, obviously, exist, for solid bodies both transmit and absorb heat. Thus they must be capable of taking up the kinetic energy from a gas and, in turn, passing on energy to a gas. A body held in a fixed position, while not free to execute random heat motions, may well move if disturbed. Such a motion will be an oscillation or a vibration about its rest position as center. Since it is likely that, within certain limits, the forces urging the displaced atom or molecule in a solid back to its initial position may be assumed to obey Hooke's law, the particles then execute simple harmonic vibrations about their equilibrium positions. Thus the heat motions in a crystal consist of vibrations of the atoms or molecules about their rest positions. Since, on the average, each such degree of freedom of harmonic vibrations has equal amounts of kinetic and potential energies, there are 2 cal. per degree C associated with each degree of freedom of vibration in a gram-molecule of solid. As there are only three degrees of freedom of vibrations possible, along the three coordinate axes, the molecular heat should be

$$MC_p = 3 \times R = 6 \text{ cal. per degree C.}$$

Thus Du Long and Petit's law that each molecule or atom has associated with it a given amount of the absorbed energy which goes to raise its temperature at once finds its explanation in terms of the kinetic theory and the law of equipartition. With the exceptions discussed before, and which will be analyzed in what follows, this law holds for the elements very closely. For complex solids the law of Neumann holds. Here it is found that each molecule often does not absorb its full 6 cal., but where certain groupings appear the energy absorbed is less. This finds immediate and simple explanation in the view now held of the crystal structure in the case of complicated molecular groupings. Thus in $CaCO_3$ the crystal is built up of Ca atoms and CO_3 groups. The latter then act as a unit. It is quite plausible to assume that each of the atoms in this CO_3 unit are not free to vibrate in all three of

their degrees of freedom. Hence it is to be expected that where the CO_3 group occurs its contribution to the molecular heat may not be 24 units, but less, owing to some of the vibrational modes suppressed in its component atoms. Why some modes are suppressed and others not is explainable on the basis of the quantum theory, for if one of the oxygen atoms is very rigidly bound to the CO_2, and not equally so bound in the group along the three axes, it will require blows of greater energy to set the particular vibration into operation—that is to say, it is possible that at the existing temperature the average kinetic energy is too low to awaken the particular mode of vibration. Hence only those vibrations which are loosely enough bound to be active at the temperature in question should respond, and the energy absorptions will be less by 2 cal. for each such "sleeping" degree of freedom. Of course, since the energy exchanges are statistical, an occasional degree that is normally "sleeping" will absorb. More of these will absorb the higher the temperature. Thus the molecular heat of such a compound will begin to go up as certain temperatures are approached. This increase will at first be gradual and then more rapid, but in any case more or less continual, due to the continuous value of the energy distribution function.

The explanation just given for the Neumann law should also apply to all the elements as well. In this case, however, the greater symmetry of the crystal lattices and the equality of the atoms should make the probability of exceptionally strong forces in certain directions less likely. As may be seen from the table on page 360, this is the case. The three elements C, Si, and B, having the highest melting points, however, deviate quite perceptibly and have MC_p well below 6 cal. This is not surprising, since the high melting points of these substances indicate very intense interatomic forces, for the melting points are merely the temperatures where the average kinetic energy of agitation of the atoms becomes comparable with the potential energies of the atoms in the crystal. At this point the interatomic forces cease to be able to hold the atoms in the rigid positions characterizing the solid and the body melts, becoming a liquid. Strong forces mean that the vibrational frequencies of the atoms are high, and thus at room temperatures the average heat impact is not able to impart $h\nu$ to all the different modes of vibration possible. As the temperature increases, this becomes possible and at higher temperatures C, Si, and B all show the normal value for MC_p. As

temperatures are lowered, all of the solid elements, and, in fact, all substances, should have decreasing values of MC_v, and at 0° abs. MC_v should be 0, for no mode of vibration can have a frequency so low as to be set into vibration at 0 energy. The accurate study of the decrease of the specific heats of the elements as the temperature was lowered was largely the work of Nernst[19] and his pupils. It was this study which most helped to lead to the explanations of the deviations from Du Long and Petit's law on the basis of the quantum theory.

At very high temperatures MC_p for the elements increases above 6 cal., and, in fact, it is so for the alkali metals at a little above room temperatures. This may be ascribed to the absorption of energy into degrees of freedom so far not included. It coincides with the emission of light by the heated solids. The equipartition of energy of motion among the atoms and molecules heretofore discussed, as was stated in Sec. 9 and 92, presupposed that no energy was absorbed into the atoms themselves, that is, it was assumed that the energy was not taken up by individual electrons of the atoms. In view of the work of Franck[13] and Hertz and all of the present-day knowledge of the quantum theory as regards the electronic energy exchanges, it is obvious that at ordinary temperatures it would not be expected that this would occur; at 1000 or 1200°C. there are four to five times the energy of agitation, so that the probability of having impacts which can excite some of the lower electronic frequencies begins to be appreciable. It is, therefore, not astonishing that MC_p should increase above 6 cal. at high temperatures.

One more point should be touched on here. In the metallic elements, electrical conduction and even heat conduction received a tentative explanation from the electronic point of view, that is, the parallelism between heat conductivity K and electrical conductivity $\frac{1}{\rho}$ of metals, which was evidenced in the Wiedeman-Franz[20] law that $K\rho$ = constant, led to a theory that these conductivities were due to the same agent. On the discovery of the electron, the high electrical conductivity of the metal conductors as against ionic conductors, such as liquids, led to the assumption that the conductivity of the metals was due to the highly mobile electron. Thus heat conductivity was also ascribed to this agent. The conductivity of heat and electricity by electrons led at that time to the assumption of the existence of large num-

bers of *permanently free electrons* in the metal which were in thermal equilibrium with the atoms of the metal. Certain phenomenon, such as the reflection of light by metals, the Peltier effect, the contact potentials, the general photoelectric effect, and the thermionic effect (mentioned in Sec. 45), also seemed to confirm the workers in this belief.[21] On the basis of such evidence, Lorentz[22] worked out an elaborate theory of electronic conduction, which was later extended by Richardson,[21] Drude,[23] Norman Campbell,[24] and others. It led, however, in its extreme form to one conclusion which was not justified by fact. In order to account for optical conductivity and Peltier effects, the actual numbers of free electrons present had to be assumed to be very large, that is to say, they were assumed to be at least comparable in number to the number of atoms present. An alternative to this was that they have mean free paths of excessive length in the metal. While the latter alternative was possible, it did not seem probable at that time. Today it is considered more likely in view of the apparent transparency of atoms like argon to slow electrons.[25] Thus at that time the assumption of large numbers of free electrons in thermal equilibrium with the metals was made. If this is so, the electrons must, if they are present in the same numbers as the atoms, contribute to the specific heat, that is, MC_p for metals must be increased by 3 cal. for the translational energies of the electrons if there are as many present as there are atoms.

It is of interest to see to what extent this condition holds true. A glance at the values of the atomic heats of the elements in the table of Sec. 90 shows that many of the elements have a heat higher than 6. Others seem to have lower ones. There, furthermore, seems to be no correlation between the electrical conductivity, or "free electron" content, and the excess value of atomic heat as the table stands. G. N. Lewis[26] and Gibson point out that for most of these substances the heat measured is not MC_v but MC_p. While the difference is small, calculation shows it to be appreciable. They obtained data which enabled $C_p - C_v$ to be computed for 15 elements. They found MC_p for iodine to be 6.9, and $MC_p - MC_v = 0.9$. Thus the true MC_v for iodine was 6.0 and not 6.9 cal. The values of $MC_p - MC_v$ calculated by them are given in the following table:

$MC_p - MC_v$

Li	0.3	Co	0.1	Sn	0.1
Be	0.2	Ni	0.2	I	0.9
C	0.0	Cu	0.2	La	0.1
Na	0.5	Zn	0.3	Ce	0.1
Mg	0.2	As	0.0	W	0.1
Al	0.2	Se	0.3	Os	0.1
Si	0.1	Zr	0.1	Ir	0.2
S	0.4	Mo	0.1	Pt	0.2
K	0.6	Ru	0.1	Au	0.3
Ca	0.3	Rh	0.1	Tl	0.3
Ti	0.1	Pd	0.2	Pb	0.4
Cr	0.1	Ag	0.3	Bi	0.1
Mn	0.1	Cd	0.3	Th	0.1
Fe	0.1	Sb	0.3	U	0.1

Using these data, they find for 15 elements a mean value of MC_v of 5.9, with the average deviation of 0.09. It is, therefore, shown that for almost all metals MC_v is nearly 6 and the electrons do not share markedly in the specific-heat contribution. Lewis, Eastman, and Rodebush,[27] however, found that for certain electropositive metals (*e.g.*, Na, K, Cu, and Mg), MC_v rose well above 6 cal. as the temperature went up. In the most electropositive element Cs Dewar[28] showed that, even between the boiling point of H_2 and of liquid air, MC_v was greater than 6 cal. This these authors interpreted as meaning that number of electrons in these metals are held in such weak restraints that they can pick up thermal energy of low value.

The verdict of this evidence, on the whole, seems to be that *in no metal are there numbers of "free" electrons closely comparable in number with the atoms of the metal.* At higher temperatures the electrons certainly partake of the energy of agitation. Thus it would seem that the specific-heat data answer the question of the old "free electron" atmosphere quite decisively, while they also indicate the presence of electrons very loosely bound.

94. Calculation of the Temperature Variation of Specific Heats from the Quantum Theory and the Values of the Natural Atomic Frequencies ν in Solids.—It is instructive to study a simple derivation of the equation for the variation of specific heat with temperature. By means of such an expression, the natural frequencies ν of the atoms may be computed and the value compared with those obtained by other methods. The derivation is also of value, as it indicates how the quantum theory operates in such cases as have been dealt with.

To achieve this, one proceeds as follows. For the sake of simplicity, assume that the oscillator or atom is a linear oscillator describing simple harmonic oscillations. From this and the general law for the distribution of energy, assuming equipartition among the infinite number of values of the energy of oscillation, one obtains, by integration, the average energy for one of the degrees of freedom of the linear oscillator, or the atom. This is an expression which is merely $\frac{2}{2}kT$ for the vibrating atom (see Sec. 36 for further details). The above is merely the application of the distribution law to the case of oscillatory instead of translatory motion. It is then necessary to introduce the quantum conditions before integrating the expression above, which was obtained for the energy before introducing the quantum concepts. Owing to the discontinuous nature of such a quantized energy content, the solution cannot be obtained by integration, but must be obtained by summing a series. The new value of the average energy per degree of freedom will then be found to be of a complicated form involving the ratio of the energy quantum and the absolute temperature.

Consider the simplest type of an oscillator, that is, an oscillator which executes simple harmonic motions along a straight line. This might be an atom bound in a crystal. The state of the atom or oscillator is defined by the coordinates x, y, and z of its center of mass, and u, v, and w of its velocity of translation. From the general law of equipartition of energy, the number of atoms of the solid with these parameters between x and $x + dx$, u and $u + du$, etc. are given by the Maxwell-Boltzmann law of equipartition. This says, in its most general form, that

$$d\eta = Ae^{-2hE}dxdydzdudvdw.$$

In this expression the $2hE$ is equivalent to $\frac{c^2}{\alpha^2}$ in the expression for the distribution of velocities on Maxwell's distribution law given in Sec. 36. E is, however, the *total energy of a linear oscillator* and is given by $E = (\frac{1}{2}m\bar{c}^2 + ad^2)$, where $\frac{m\bar{c}^2}{2}$ is the kinetic energy and ad^2 is the potential energy, a being the force constant and d the displacement.

It is simpler to consider the energy along one axis only, since the energies, on the average, are equal along the three axes. This is equivalent to picking one degree of freedom of oscillation only. To get this from the above expression one must integrate

it for all values of y, z, v, and w. This gives $d\eta_x$, the number of atoms or oscillators with parameters beween x and $x + dx$, and u and $u + du$ only, as

$$d\eta_x = A_x e^{-2hE_x} dx du,$$

where

$$E_x = \left(\frac{1}{2}mu^2 + ax^2\right).$$

Putting $h = \frac{1}{2kT}$, where k is the Boltzmann constant (see Sec. 42), then,

$$d\eta_x = A_x e^{-\frac{E_x}{kT}} dx du.$$

This cannot be integrated in this form, for u and x must be expressed in the same form as E_x, that is, to integrate this equation it must be transformed from an area in the ux plane to an area in polar coordinates in the E_x plane. Since $E_x = \frac{1}{2}mu^2 + ax^2$, one may choose as axes $\sqrt{\frac{m}{2}}u$ and $\sqrt{a}x$. Then $\sqrt{E_x}$ becomes the radius of a circle, and the result is:

$$\sqrt{\frac{m}{2}}u = \sqrt{E_x} \sin \theta$$

$$\sqrt{a}x = \sqrt{E_x} \cos \theta.$$

By means of a Jacobean transformation the area $dudx$ may be transformed into an area in the E_x, θ plane.

$$dudx_\theta = \begin{vmatrix} \sqrt{\frac{m}{2}}\frac{\partial u}{\partial E_x} & \sqrt{\frac{m}{2}}\frac{\partial u}{\partial \theta} \\ \sqrt{a}\frac{\partial x}{\partial E_x} & \sqrt{a}\frac{\partial x}{\partial \theta} \end{vmatrix} \frac{dE_x d\theta}{\sqrt{\frac{am}{2}}}$$

$$\sqrt{\frac{m}{2}}\frac{\partial u}{\partial E_x} = \frac{1}{2E_x^{1/2}} \sin \theta$$

$$\sqrt{\frac{m}{2}}\frac{\partial u}{\partial \theta} = E_x^{1/2} \sin \theta$$

$$\frac{\sqrt{a}\,\partial x}{\partial E_x} = \frac{1}{2E_x^{1/2}} \cos \theta$$

$$\sqrt{a}\frac{\partial x}{\partial \theta} = -\sqrt{E_x} \sin \theta$$

$$dudx_\theta = \left(-\frac{E_x^{1/2}\sin^2\theta}{2E_x^{1/2}} - \frac{E_x^{1/2}\cos^2\theta}{2E_x^{1/2}}\right)\frac{dE_x d\theta}{\sqrt{a\frac{m}{2}}} = -\frac{1}{2}\frac{dE_x d\theta}{\sqrt{a\frac{m}{2}}}.$$

Therefore $$dudx_\theta = -\frac{1}{2}\frac{dE_x d\theta}{\sqrt{\frac{am}{2}}}.$$

For all values of θ, $dudx$ becomes

$$dudx = -\frac{1}{2}\frac{dE_x}{\sqrt{\frac{am}{2}}}\int_0^{2\pi}(d\theta).$$

Hence $$dudx = -\frac{\pi d(E_x)}{\sqrt{\frac{am}{2}}}.$$

From this it follows that

$$d\eta_x = d\eta_{E_x} = Be^{-\frac{E_x}{kT}}dE_x,$$

where $$B = -\frac{\pi A_x}{\sqrt{\frac{am}{2}}}.$$

Now if any value of the energy is equally probable for linear vibration, that is to say, the energy is not quantized or distributed in any other manner, the average energy possessed by a degree of freedom may at once be calculated from

$$\overline{E}_x = \frac{\int_0^\infty E_x d\eta_{E_x}}{\int_0^\infty d\eta_{E_x}}$$

that is $$\overline{E}_x = \frac{B\int_0^\infty E_x e^{-\frac{E_x}{kT}}dE_x}{B\int_0^\infty e^{-\frac{E_x}{kT}}dE_x}$$
$$= kT,$$

that is, for a linear oscillator the energy per degree of freedom is kT. For three degrees of freedom it is $3kT$. If it be multiplied by N_A and differentiated for T, then at once $MC_v = N_A\frac{dE}{dT}$ $= 3N_A\frac{dE_x}{dT} = 3kN_A = 3R$, or 6 calories. This is independent of T and is merely the expression obtained for MC_v before on elementary considerations. Now actually, if it is assumed

that the energy can only be absorbed in quanta, in which the quanta must be equal to a given value depending on the frequency of the oscillator, it is impossible to integrate in the manner above. The situation may be seen in the two diagrams of Fig. 53. Diagram *a* gives the distribution law for energy E_x among the oscillators, assuming all energies are possible. The average E_x is obtained by the integration process performed above. It

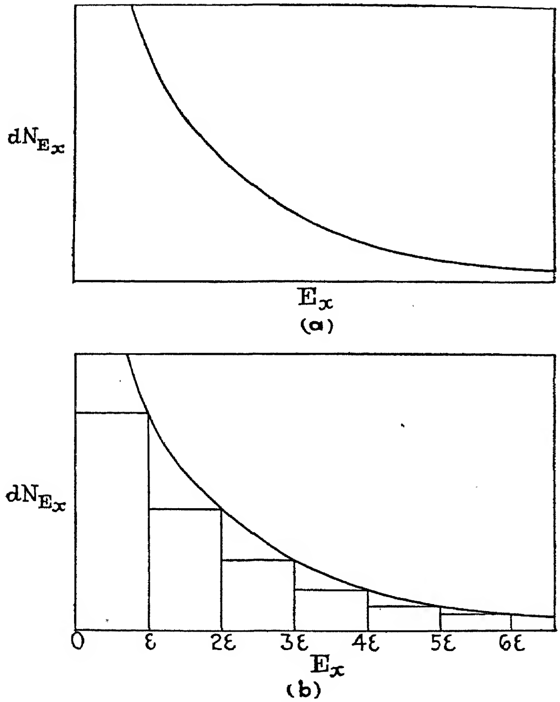

FIG. 53.

is the product $E_x d\eta_{E_x}$ summed up from 0 to ∞, divided by $d\eta_{E_x}$ integrated from 0 to ∞, that is, by the total number of atoms in each element summed up for all the elements. In the diagram *b* the curve is not continuous but the total energy content is made up of the various strips $dE_x = \epsilon$ wide and having consecutively the ordinates $d\eta_{E_x}$ given for the particular strip ϵ in question. The E_x is then the sum of a finite number of the quantities ϵ, of value, respectively, 0, ϵ, 2ϵ, 3ϵ, 4ϵ, etc. the number of atoms having the energy E_x being given by the appropriate

value of $d\eta_{E_x}$ for the given energy ϵ, 2ϵ, 3ϵ, 4ϵ, etc. The quantity previously represented by

$$\int_0^\infty d\eta_{E_x} \text{ is now} \sum_0^\infty d\eta_{E_x}$$

$$= B\left[\epsilon e^{-\frac{0}{kT}} + \epsilon e^{-\frac{\epsilon}{kT}} + \epsilon e^{-\frac{2\epsilon}{kT}} + \ . \ . \ . \ \right],$$

for the value of $d\eta_{E_x} = Be^{-\frac{Ex}{kT}}dE_x$, and E_x has progressively the values 0, ϵ, 2ϵ, 3ϵ, etc. while $dE_x = \epsilon$, and that represented by

$$\int_0^\infty E_x d\eta_{E_x} \text{ is now} \sum_0^\infty E_x d\eta_{E_x}$$

$$= B\left[o \times \epsilon e^{-\frac{0}{kT}} + \epsilon \times \epsilon e^{-\frac{\epsilon}{kT}} + \epsilon \times 2\epsilon e^{-\frac{2\epsilon}{kT}} + \epsilon \times 3\epsilon e^{-\frac{3\epsilon}{kT}} \ . \ . \ . \right]$$

$$\text{Therefore } \overline{E}_x = \frac{B\left[0 + \epsilon^2 e^{-\frac{\epsilon}{kT}} + 2\epsilon^2 e^{-\frac{2\epsilon}{kT}} + 3\epsilon^2 e^{-\frac{3\epsilon}{kT}} + \ . \ . \ . \ \right]}{B\left[\epsilon + \epsilon e^{-\frac{\epsilon}{kT}} + \epsilon e^{-\frac{2\epsilon}{kT}} + \epsilon e^{-\frac{3\epsilon}{kT}} + \ . \ . \ . \ \right]}.$$

This leads to the study of the power series obtained by setting $x = e^{-\frac{\epsilon}{kT}}$ and gives an expression

$$\overline{E}_x = \frac{\epsilon x}{(1 - x)}, \text{ or } \overline{E}_x = \frac{\epsilon}{e^{+\frac{\epsilon}{kT}} - 1}.$$

To get the specific heat, this must be differentiated with respect to T. Differentiation gives

$$\frac{d\overline{E}_x}{dT} = \frac{k\epsilon^2 e^{\frac{\epsilon}{kT}}}{\left(e^{\frac{\epsilon}{kT}} - 1\right)^2}.$$

For a gram-molecule, that is, for N_A molecules and for three degrees of freedom, one has MC_v for a monatomic gas as

$$MC_v = N_A \frac{3d\overline{E}_x}{dT} = \frac{d\overline{E}_{N_A}}{dT} = \frac{3R\epsilon^2 e^{\frac{\epsilon}{kT}}}{\left(e^{\frac{\epsilon}{kT}} - 1\right)^2}.$$

The energy quantum ϵ according to the quantum theory is $h\nu$, where ν is the characteristic frequency of the atoms and h is the Planck constant. Thus one may write that

$$MC_v = 3R\frac{h^2\nu^2 e^{+\frac{h\nu}{kT}}}{\left(e^{\frac{h\nu}{kT}} - 1\right)^2}.$$

It is seen that when $\frac{h\nu}{kT}$ is very large, that is, T is very small, this quantity is nearly 0, and asymptotically approaches 0 as T approaches 0. When kT is large compared to $h\nu$, this quantity approaches $3R$ asymptotically. Since $3R$ is the classical value for C_v, the equation fits the experimental facts quite well.

The values of ν found from the form of the experimental curves makes it possible to plot the theoretical curves and to compare them with the observed curves. The comparison leads to a satisfactory agreement. As a final check on this theory, the comparison of the value for ν obtained from the experimental results, using this equation, may be compared with other estimates of ν.[33]

Since ν is a characteristic of the atoms in the crystal structure, and is related to the forces of restitution for the atoms in the body, it is not surprising to find that Einstein[29] as far back as 1911 found a relation between ν and the elastic properties of the body. On the assumption that the atom vibrates with simple periodic vibrations (*i.e.*, that it emits monochromatic waves) he derived an expression for

$$\nu_E = \frac{2.8 \times 10^7}{A^{1/3}\rho^{1/6}K^{1/2}},$$

where A is the atomic weight, ρ the density, and K the compressibility of the body. Lindemann[31] assumed that the amplitude of the atomic vibrations in a solid at the melting point is of the order of the distance between the atoms. From this assumption he obtained the following relation between T_S the absolute melting point and the characteristic frequency ν

$$\nu_{T_S} = 2.8 \times 10^{12}\frac{T_S{}^{1/2}\rho^{1/3}}{A^{5/6}},$$

where A and ρ have the same significance as before. It is seen at once why the light refractory elements at room temperature depart from the Du Long and Petit law so widely, for with a small A and a large T_S, ν_{T_S} is very great, which makes $C_v < 3R$ in the equation above. Finally, E. Madelung[30] and W. Sutherland,[32] independently, found that in certain substances the frequency ν should coincide with the optical frequencies of the atoms. Thus rock salt, Sylvin (KCl), and KBr show strong absorption bands in the far infra-red. Together with this they show strong metallic reflection for these same waves. Thus these crystals have atoms which have natural frequencies in this region. These frequencies

can be none other than the oscillation frequencies of the atoms in these bodies, for the crystal is known to be composed of a regular lattice in which the metal ion and the anion alternate. Thus as these electric waves have too low a frequency to be electronic in origin, they can only come from the oscillations of the *charged atoms* or *ions* themselves. Since these are the atoms, the atomic frequency ν must be the same as these. Now by repeated selective reflection from a rock salt or other crystal, these waves can be segregated out and their wave lengths measured. Thus one can find ν for the atoms directly by getting the wave length of the residual rays according to Nernst.[34] The comparison of these values with the values from the atomic-heat equation may be seen summarized for a few substances. The first column gives the element or substance used; the second, ν_E calculated from elasticity data, using Einstein's equation; the third the value of ν_{T_S} calculated by the Lindemann formula from the absolute melting point. Column four gives ν_R for the residual rays and the last column the values of ν calculated from the atomic or molecular heats by Lindemann and Nernst from the equation for specific heats. Thus the values for ν from the equation agree in a remarkable fashion with the values of ν calculated from diverse sources with approximate equations. They thus give an excellent confirmation to the theory of atomic heats as modified by the new quantum concepts.

CHARACTERISTIC FREQUENCY

Substance	ν_E	ν_{T_S}	ν_R	$\nu_{\text{atomic heat}}$
Al	6.7×10^{12}	7.6×10^{12}	....	8.3×10^{12}
Cu	5.7×10^{12}	6.8×10^{12}	....	6.7×10^{12}
Zn	....	4.4×10^{12}	....	4.8×10^{12}
Ag	4.1×10^{12}	4.4×10^{12}	....	4.5×10^{12}
Pb	2.2×10^{12}	1.8×10^{12}	....	1.5×10^{12}
Diamond	....	32.5×10^{12}	....	40.0×10^{12}
NaCl	....	7.2×10^{12}	5.8×10^{12}	5.9×10^{12}
KCl	....	5.6×10^{12}	4.7×10^{12}	4.5×10^{12}

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b. REICHE, E.: *Loc. cit.* An excellent review of literature and general summary of the quantum theory.
c. SOMMERFELD: *Loc. cit.* For quantum theory and atomic structure.
d. FRANCK, J.: *Loc. cit.*, vol. 2, 1923. For elasticity of impact and emission of light.
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CHAPTER X

CONTRIBUTIONS OF THE KINETIC THEORY TO ELECTRICAL AND MAGNETIC PROPERTIES OF MOLECULES

I. THE DIELECTRIC CONSTANT OF MOLECULES

95. Elementary Statement of the Problem.—It had long been known that there was a relation between the optical refractive index of a substance and its chemical nature. In fact, Gladstone and Dale[1] as far back as 1858 to 1863, and Landolt[2] found that the refractive index n diminished by unity and divided by the density ρ gave a characteristic quantity associated with each chemical type of atom. This when applied to the atoms of some compounds had marked additive properties. It did not hold for changes of state of aggregation nor did it fulfil the values observed in mixtures very well. An equation was deduced simultaneously in 1880 by Lorenz[3] in Copenhagen and Lorentz[4] in Leyden on a sound theoretical basis which satisfied the condition of being independent of the state of aggregation quite well. It starts out with the assumption that the molecules are spherical electrical conductors. If such molecules find themselves in an electrical field they will have charges induced on them of opposite signs on the two sides of the plane normal to the line represented by the direction of the field and passing through the center, that is, the centers of gravity of the positive and negative electricity present in equal amounts will be shifted from the center of the sphere by the field, so that the molecules act as induced electrical dipoles. Such dipoles would act on the charged bodies producing the field so as to diminish the forces between them, and it is thus that the dielectric constant may be accounted for. Clausius[5] had shown in 1867 that if the fraction of the volume occupied by the substance which is actually occupied by the molecules be u, then the dielectric constant δ is given by an expression $\delta = \frac{1 + 2u}{1 - u}$. This expression will be deduced in a later section. Thus the

fraction of the volume of a gas occupied by the molecules themselves will be given by

$$u = \frac{\delta - 1}{\delta + 2}.$$

For a gram-molecule of substance M, of density ρ, the total volume is $\frac{M}{\rho}$. Then if P_0 is the fraction of the volume occupied by the molecules in a gram-molecule, one may write

$$P_0 = \frac{uM}{\rho} = \frac{\delta - 1}{\delta + 2}\frac{M}{\rho}.$$

This P_0 is termed the polarizability and is independent of the density.

Now from the wave theory of light it had been known that δ should approximate n^2, the refractive index, particularly where n^2 could be measured far from an absorption band, or for very long wave lengths when there are no absorption bands in the infra-red. Thus for a gram-molecule where n is the index of refraction, one can write P, the specific refraction:

$$M\frac{u}{\rho} = P = \frac{n^2 - 1}{n^2 + 2}\frac{M}{d}.$$

The result is an equation representing the relation of the index of refraction to the actual specific volume of the molecule which is supposed to act like a conducting sphere. This should depend on the characteristics of this molecule only and represent its contribution to the refractive index no matter what the state of aggregation. The theory achieved a remarkable amount of success in its applications, and the success achieved may be seen in referring, for instance, to Nernst's[6] "Theoretical Chemistry," Seventh Edition, Chap. VI.

As was seen above in deducing the Lorentz-Lorenz law, which holds surprisingly well, an expression for u in terms of δ, the dielectric constant, was first deduced, on the Clausius-Mosotti theory of dielectrics. This expression *should have the same validity as the expression for the index of refraction which was deduced from it.* Thus since n^2 was assumed equal to δ, the additive law for refractivity should also hold for the dielectric constants δ, that is, P_0 which holds for infinitely long electric waves should be given by $P_0 = \frac{\delta - 1}{\delta + 2}\frac{M}{\rho}$. This is, however, found to be in no sense the case. For some substances the value of P_0 is not at all

constant with the temperature or varying state of aggregation. It also fails for the case of mixtures, and the additive laws found in the case of the index of refraction cannot possibly be applied to some substances. It was at first thought that this was due to the fact that for some substances n^2 did not equal δ, as, owing to absorption bands, the extrapolation of n^2 for visible light did not give the real value in the infra-red (see Nernst, *Loc. cit.*). As investigations in the spectra developed, this explanation of the failure did not seem to agree with the facts and the matter remained unexplained. In 1912, Debye[7] published a paper in which the idea which lay at the basis of his beautiful explanation was expounded. It was further developed in subsequent papers and a masterful account of this will be found in his chapter on the subject in Marx's "Handbuch der Radiologie,"[8] from which a large portion of the subsequent discussion in a simplified form was taken.

To understand Debye's reasoning, one must return to the underlying Clausius-Mosotti picture of the molecules from which their equation was deduced. The molecules were assumed to be conducting spheres which could not give up their charges on contact but were charged on opposite sides by the inducing field. These by their action led to an expression between u, their total volume, and the dielectric constant δ of the form given before; namely,

$$u = \frac{\delta - 1}{\delta + 2}.$$

For those in a gram-molecule the volume should be $P_0 = \dfrac{\delta - 1}{\delta + 2}\dfrac{M}{\rho}$, that is, the actual volume of the spherical conducting molecules in a gram-molecule should be given by P_0. Now from Van der Waals' equation (Sec. 48) one has a quantity b whose volume is four times the total volume of the molecules present. Thus b should equal $4P_0$ calculated from the above equations. Actually, from critical data $b = \dfrac{V_c}{3}$ or $P_0 = \dfrac{1}{12}V_c$. From the critical data also $\dfrac{p_c v_c}{RT_c} = \dfrac{3}{8}$ (see Sec. 52), so that

$$P_0 = \frac{1}{32}\frac{RT_c}{p_c}.$$

The values of P_0 computed from δ for O_2, H_2, and NH_3 gases are given in the table and compared with the values calculated from

the critical data. For H_2, $P_0 = \frac{1}{12} V_c$ was used as it was for the first value of O_2. For the second value of O_2 used, as well as for NH_3, the expression

$$P_0 = \frac{1}{32} \frac{RT_c}{p_c}$$

was used as the latter data are better for NH_3.

Gas	P_0 by δ	P_0 critical data
H_2	2.04	4.98
O_2*	4.05	6.20
O_2	4.05	7.83
NH_3	63.0	9.52

* The difference in the figures for O_2 is due to errors inherent in all calculations from critical data (see Sec. 52).

The table is very interesting as it shows first that for H_2 and O_2 the value of P_0 obtained, assuming that the atoms act as conducting spheres, is in as good an agreement as can be expected with observed values of the volumes. For NH_3 this is not the case. The disagreement is striking, being almost one of order of magnitude. Again, the constant P_0 should be additive, as it is for the case of P, using refractive indices. This is found to be the case for carbon and hydrogen in CH_4 and C_6H_6. For H_2, P_0 was 2.04 cm³, so that for H it is 1.02 cm³. For CH_4 one calculates, from δ, $P_0 = 7.09$ cm³, whence if the additive law holds P_0 for carbon should be 3.01 cm³. Benzene (C_6H_6) leads one to calculate P_0 on the additive law from P_0 for carbon and hydrogen as 24.2 cm³. The observed value is 27.5 cm³. Thus for carbon and hydrogen the additive laws for P_0 calculated from δ seem to hold in CH_4 and C_6H_6. For N_2, P_0 is 4.33 cm³ from δ, so that N has P_0 as 2.16 cm³ if the additive law holds for N_2, as appears to be the case. Calculating P_0 for NH_3 from these data on an additive law, it comes out 5.22 cm³. The P_0 as computed from the observed δ is 63 cm³. Thus again NH_3 fails to obey the additive law, while H, N, C, and O seem to follow it in some compounds.

Finally, if the variation of P_0 with temperature is examined under conditions where the molecules are separated by considerable distances as in a gas or in dilute solutions, it will be found that a large number of them have P_0 constant with temperature, as the theory demands. These substances comprise the whole

group found above that give the values of P_0 from δ which agree with other data, and that follow the additive law, *e.g.*, O_2, N_2, H_2, CH_4, C_6H_6. On the other hand, substances like NH_3, SO_2, H_2O, alcohols, pyridine, etc., which fail to give reasonable values of P_0 from δ and do not follow the additive law, also show a large variation of P_0 with T. Thus for NH_3, P_0 decreases as the temperature increases, as seen in the table below:

T	P_0
292.2	57.57
309.0	55.01
333.0	51.22
387.0	44.99
413.0	42.51
446.0	39.59
448.0	39.50

All these phenomena appeared to Debye to have a common cause, and he asked the question, How can one have a dielectric constant or a portion of it that varies with the absolute temperature? This at once leads one back to the original Clausius-Mosotti explanation of δ. According to them, δ was due to the polarization of electrically conducting spherical molecules. Debye and others investigated this in the light of modern theories of atomic structure and found that the type of action assumed by Clausius and Mosotti for their conducting spheres was also applicable to molecules composed of nuclei with orbital electrons. Debye, however, could imagine no mechanism for this type of polarizing action consistent with modern theory which would account for a temperature variation. If, however, it is assumed that with this polarizability there exist in some of the molecules permanent electrical dipoles the case is entirely different. The precedent for this idea lay in the fact that the chemists had long regarded the electrical charges of substances strongly ionized in aqueous solutions to be segregated even in the molecules. This was required to account for the easy electrolytic dissociation. Thus, for instance, in HCl the H atom was supposed to be positively charged and the Cl atom negatively charged. The HCl molecule has thus a permanent electrical moment as the H and Cl atoms are separated by finite distances from each other in the molecule. With permanent dipoles the whole temperature effect is explained as well as the high non-additive values of P_0. The idea for this explanation came to Debye from the work of Langevin, who had in 1905 deduced the expression for the

magnetic behavior of paramagnetic gases as a function of the temperature, assuming the existence of molecular magnetic dipoles, for if HCl molecules are imagined in a gas the action of a field will be such as to cause the molecules to try to orient themselves in the field. This orientation analogously to the case of molecular magnets in iron in a magnetic field tends to be destroyed by the random heat motions. Thus, although the HCl molecules are free to turn in the field, on the average, they are oriented only partially in the field and only a fraction of the moment is effective. This could be expressed by the moment multiplied by the cosine of the average angle of orientation in the field. The higher the temperature the less the orientation and hence, as the temperature increases, the value of δ, and so the apparent value of P_0, should decrease. Again, the Clausius-Mosotti equation allows one to calculate only the induced portion of P_0. Thus the values of P_0 due to the induced electrification of separate atoms in a compound should really be less than values of P_0 calculated from a δ where part of this quantity is due to permanent moments. This explains the non-additive nature of the values of P_0 for such compounds. While N and H separately have a small additive P_0 due to induced electrification of the Clausius-Mosotti type when they unite to form NH_3, there is a new grouping with a large permanent dipole moment due to the segregation of the charges in this particular type of molecule. Other compounds of H and N which did not have this could conceivably have a δ and hence a P_0 where the H and N P_0 values combined purely additively and were of a simple induced nature. Most compounds have a P calculated from the index of refraction which is nicely additive, since, because of the very high frequency of the light vibrations, the slow orientation of the permanent molecular dipoles in the field cannot occur. Hence here mostly the purely induced dielectric constants which are nicely additive are dealt with. In certain cases where the frequencies of the light waves approach frequencies of dipole rotation in the infra-red this no longer holds and the additivity then begins to break down.

This beautiful explanation of the paradoxical situation of the two equations of $P_0 = \frac{\delta - 1}{\delta + 2}\frac{M}{\rho}$ and $P = \frac{n^2 - 1}{n^2 + 2}\frac{M}{\rho}$, where the second equation held while the one from which it was derived failed, merits treatment in this book because of its relation to the kinetic theory. It is also very desirable that it be made accessi-

ble to students in this country to whom it would otherwise be inaccessible due to language difficulties and to the fact that it does not appear in usual reference books. In the succeeding sections the Clausius-Mosotti equation will be deduced and the Debye calculation for the temperature variation of δ will be given. Section 97 will give the beautiful quantitative agreement between theory and experiment. In Part II, the treatment of the magnetic properties of gases from a similar point of view will be given.

96. Theory of the Variation of Dielectric Constant with Temperature. *a. The Deduction of the Clausius-Mosotti Law.*—Consider a region in free space with no material present and produce an electrical field E in this region; the field produced has the intensity E, that is, if one represent it by the number of lines of force per cm^2 normal to the direction of these lines, there will be E lines of force per cm^2. If, now, one place matter in this space, the field intensity will no longer be E, but it will have the value D. D is, however, related to E in a simple manner. Owing to the presence of induced electrical charges in the dielectric, the added lines of force can be treated as coming from the two ends of the volume considered, the ends being chosen normal to the lines of force, that is, the action of this region filled by matter can be imagined as being replaced by two condenser plates with a charge density at the two ends of the volume. This new charge gives lines of force which add to the field E initially existing. If unit volume is considered, these charges may be designated as $\pm P$. Hence, numerically, each unit volume will contribute $4\pi P$ new lines to the field E. Thus D, the dielectric displacement, is given by

$$D = E + 4\pi P,$$

where P is called the polarization. Now P is proportional to E in certain cases, for P is caused by E. Thus $P = KE$, where K is the electrical susceptibility. For the cases where this holds then

$$D = E(1 + 4\pi K).$$

This may be written in a different form, to wit, $D = \delta E$, where $\delta = 1 + 4\pi K$ and is known as the dielectric constant. It is the same quantity by which the force between two electrified bodies in a medium is reduced by the polarization of the medium. Thus it is δ which is measured experimentally, and the quantity K must be derived from it.

All the above considerations apply to the case of a homogeneous medium filled uniformly with matter of dielectric properties. Actually, matter is made up of molecules whose total volume may make up only a fraction of the total volume. The question of interest is how these molecules affect the dielectric constant, and what can be learned about the molecules by a study of their dielectric constants. It could be assumed that for any one molecule the relations of the last paragraph were applicable. This molecule does, however, not find itself in an isolated space in a field E devoid of matter. It is, in fact, surrounded on all sides by molecules, each of which is polarized and each of which consequently contributes to the field acting. The field in which a molecule finds itself is not now E, but a field F. This F may also be considered proportional to E, so that one may write

$$F = E + \nu P.$$

This field will be designated as the *inner field*. The constant factor ν is called the constant of the inner field. It is a pure number which replaces the 4π in the equation above. Its value depends on the nature and distribution of the molecules. Calculations for which there is no space in this book make it possible to determine ν. For a more complete treatment, refer to H. A. Lorentz,[9] and a complete summary of the literature will be found given by Born.[10] For spherical molecules which constitute the corners of a regular molecular (or atomic) space lattice, or for such molecules which are distributed completely at random in space, (*e.g.*, as in a gas or a liquid), this factor ν is $\frac{4\pi}{3}$. Thus instead of D one now uses the inner field F, given by $F = E + \frac{4\pi}{3}P$ for cases which are of interest in the questions raised.

In the electrical case saturation as observed in ferromagnetic substances is hardly detectable.* Thus it may be assumed that a molecule in an inner field F will acquire a moment m whose average value with time $\overline{m}$ is proportional to F. Hence $\overline{m} =$

* The reason for this is that the electric fields are so feeble compared to the atomic electrical fields that the polarization produced is very slight, thus, as in magnetism, one can assume proportionality for weak fields through narrow ranges. Furthermore, the orienting action of the weak electrical fields on molecular dipoles in gases and liquids is too slight with the violent heat motions to give saturation.

γF. If there are in unit mass of the substance z molecules, and if the density is ρ, then

$$P = \rho z \overline{m} = \gamma \rho z F.$$

As, however,

$$F = E + \nu P$$

$$P = \frac{\rho z \gamma}{1 - \nu \rho z \gamma} E,$$

and

$$K = \frac{\rho z \gamma}{1 - \nu \rho z \gamma},$$

and therefore

$$\delta = 1 + 4\pi K = \frac{1 - (\nu - 4\pi)\rho z \gamma}{1 - \nu \rho z \gamma}.$$

These equations relate K and δ to ν and the polarizability of a single molecule γ. One may also put this in the form

$$\frac{\delta - 1}{\delta - \dfrac{\nu - 4\pi}{\nu}} = \nu \rho z \gamma,$$

by solving for $\rho z \gamma$. For the case where $\nu = \dfrac{4\pi}{3}$ the solution then becomes

$$\frac{\delta - 1}{\delta + 2} = \frac{4\pi}{3} \rho z \gamma.$$

If γ, the polarizability, is a constant independent of pressure or temperature, the quantity $\dfrac{\delta - 1}{\delta + 2}$ is by the equation proportional to the density. Where $\dfrac{\delta - 1}{\delta + 2}$ is not proportional to the density, that is, where $\dfrac{1}{\rho} \dfrac{\delta - 1}{\delta + 2}$ is not a constant, it is to be inferred that γ, the polarizability, varies with the temperature or pressure. That this actually occurs was noted in the Introduction, for δ is a function of the temperature. It was the study of this temperature variation which led Debye to the assumption of molecular dipoles. The above expression is the Clausius-Mosotti law.* To obtain the Lorenz-Lorentz expression from this, it

* In the deduction here, however, the conducting sphere hypothesis is absent. Clausius and Mosotti deduced the law and calculated the factor $\nu = \dfrac{4\pi}{3}$ for the special case of a conducting sphere. The deduction here is correct for any body with positive and negative charges that are relatively mobile and for the cases of random or special spatial distribution.

need only be remembered that $\delta = n^2$, where n is the index of refraction, if one is far from an absorption band and at infinite wave length. Thus one can write

$$\frac{1}{\rho}\frac{\delta - 1}{\delta + 2} = \frac{4\pi}{3}\gamma z,$$

and

$$\frac{1}{\rho}\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3}\gamma z,$$

as the Clausius-Mosotti and Lorenz-Lorentz equations. To make them more useful, both sides may be multiplied by the molecular weight M. Then

$$\frac{M}{\rho}\frac{\delta - 1}{\delta + 2} = \frac{4\pi}{3}\gamma N_A,$$

and

$$\frac{M}{\rho}\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3}\gamma N_A,$$

where N_A, the Avogadro number, is Mz. Thus the molecular refraction is a constant times the molecular polarizability. Call $\frac{4\pi}{3}\gamma N_A$ as deduced from the refractivity P, and the value deduced for the dielectric constant (*i.e.*, for infinitely long waves) P_0; then

$$P_0 = \frac{\delta - 1}{\delta + 2}\frac{M}{\rho},$$

and

$$P = \frac{n^2 - 1}{n^2 + 2}\frac{M}{\rho}.$$

The P should be equal to P_0 if for high-frequency waves and infinitely long waves δ is a constant independent of temperature. As was stated before, the law for polarizability seems to hold for fast vibrations (*i.e.*, for the equation for P), but does not hold for the equation from which this was deduced (*i.e.*, the P_0 equation).

The quantity P_0 has the dimensions of a volume. Its meaning in this sense becomes evident if one takes the earliest Clausius-Mosotti theory which assumes the molecules as conducting spheres of radius a, which do not lose their charges on contact. The moment m of such a sphere in a field F is then merely

$$m = a^3F.$$

Since $\bar{m} = \gamma F$, one obtains for this case

$$\gamma = a^3;$$

whence,

$$P_0 = \frac{4\pi}{3} N_A a^3.$$

But $\frac{4}{3}\pi a^3$ is the volume of a sphere of radius a, and N_A times this is simply the total volume of these supposed spherical molecules in a gram-molecule, that is, $P_0 = \Omega = \frac{b}{4}$, where Ω is the volume of all the molecules in a gram-molecule, and b is the b of Van der Waals' equation for a gram-molecule. As will be seen by referring to the preceding section, these predictions are fulfilled for certain substances but fail badly for others. Since, again, Ω is a constant for each type of atom, it should follow an additive law for compounds. It is found that this holds for the same substances for which computed from δ agrees with the values from Van der Waals' equation, but not for the others. The Lorenz-Lorentz equation fits fairly well for all substances in spite of the fact that it was derived from the Clausius-Mosotti law for δ which breaks down. It was the fact that the substances for which the Clausius-Mosotti law fails show a temperature variation of Ω (*i.e.*, for which γ is not independent of pressure and temperature) that Debye used in discovering the clue to the discrepancy.

b. The Temperature Variation of the Dielectric Constant.—On the basis of the preceding difficulties, Debye began to investigate the cause of a temperature variation of γ and hence P_0. The first question investigated was whether the modern views of atomic structure can cause the modifications required. The atom or molecule is considered a dynamical system of charges. If the average positions of the charges are disturbed by some external force, these charges endeavor to return to their average positions again. Investigations show that it makes no difference whether these charges are dynamical or static systems. It was also found that the sharing of the heat motions of the molecules by the electronic charges would make no difference in the law of force. As is seen (Sec. 91), this does not occur in molecules at ordinary temperatures, so that even if it did have an effect the question would not be solved. Another way out might be that it be assumed that the electrons are unsymmetrically bound to their rest positions as a second approximation, so that the potential energy of the charge on a displacement ξ would be repre-

sented by $\frac{f}{z}\,\xi^2 + \frac{g}{z}\,\xi^3$, where f and g are constants of the elastic forces. Then if the electrons shared in the heat motions, the change of dielectric constant with temperature would result. As said before, however, such an interpretation is contrary to the verdict from specific-heat considerations, and so will have to be discarded. For solids where thermal expansions change the elastic forces, and hence could change the displacements, these considerations would, of course, be applicable.

If it be assumed that the dielectric constant has, in part, another origin than the simple induced dipoles due to the displacement of the charges by the field, the whole problem is simplified. If, for instance, certain molecules like HCl have permanent dipoles present, then their dielectric constant is composed of two types of action. There is the usual further separation of the charges by the field, which has no temperature effect, and was calculated by the Clausius-Mosotti relation. This can, for the present, be ignored. The fixed dipoles in the molecules which are oriented in all directions because of thermal agitation suffer torques in the electrical field, that is, they tend to set themselves parallel to the field. This orientation is continually destroyed by the heat impacts. But, on the average, there is a resultant component of these dipoles in the field and they act to increase the dielectric strength of the material, that is, they contribute to the polarizability of the molecules. The higher the temperature, and hence the thermal agitation, the less this orientation. Thus the polarizability must decrease as temperature increases. To investigate this, one may neglect the Clausius-Mosotti type of action, and consider the charges as undisplaceable. Let the position of one of the e_i charges composing the molecule be given by its coordinates ξ_i, η_i, ζ_i along the axes x, y, z of a coordinate system in the molecule. The molecule in an electrical field of potential ϕ will have the potential energy $u = \sum e_i\phi_i$. Inside the molecule, in general, it will be possible to determine the ϕ_i in terms of its development in a power series of the coordinates ξ, η, ζ. By taking only the linear terms of these expressions, the assumption of a homogeneous field inside the molecule is introduced. If this assumption is made for simplicity, then

$$\phi_i = \phi + \xi_i\frac{\partial\phi}{\partial x} + \eta_i\frac{\partial\phi}{\partial x} + \zeta_i\frac{\partial\phi}{\partial x},$$

where ϕ, $\frac{\partial \phi}{\partial x}$ are taken relative to the origin of the coordinate system of axes chosen. For the energy u then

$$u = \phi \sum e_i + \frac{\partial \phi}{\partial x} \sum e_i \xi_i + \frac{\partial \phi}{\partial x} \sum e_i \eta_i + \frac{\partial \phi}{\partial z} \sum e_i \zeta_i.$$

If the molecule as a whole is uncharged, the $\phi \sum e_i$ term is 0, and the following three terms represent the scalar product of the field strength F and the electrical moment m. Thus without displacement of charges there is, in general, a potential energy

$$u = -(mF).$$

To compute the temperature effect, all that is needed is to assume molecules with a fixed moment of absolute value μ. From the classical kinetic theory, there will be equilibrium between the potential energy of these dipoles in the electrical field and the kinetic energy of agitation. Thus the number of molecules which have a potential energy of the value u, that is, whose potential energy in the field is $u = -m\ F = -\mu F \cos \theta$ (where θ is the angle between m and F), is given by the Maxwell-Boltzmann law, (see Sec. 36), as

$$Ae^{-\frac{u}{KT}} d\Omega = Ae^{\frac{\mu F \cos \theta}{KT}} d\Omega,$$

where $d\Omega$ represents the space-angle element of volume characterizing this energy. Thus each molecule has a moment $\mu \cos \theta$ in the direction of the field and the distribution law (see Sec. 35) gives one the number of molecules having moments for each value of θ. The average moment, that is, the moments for all the different angles of orientation averaged in terms of their probability of appearance, can be found very easily as

$$\bar{m} = \frac{\int_0^\pi e^{\frac{\mu F}{KT} \cos \theta} \mu \cos \theta d\Omega}{\int_0^\pi e^{\frac{\mu F}{KT} \cos \theta} d\Omega}.$$

If one set $\frac{\mu F}{KT} = x$, integration gives

$$\frac{\bar{m}}{\mu} = \cot x - \frac{1}{x} = L(x).$$

This function, represented in Fig. 54, plotted against x is named the Langevin function, after P. Langevin, who first applied it in

explaining the Curie law for magnetism. It may be approximated for large values of x by the power series

$$L(x) \doteq 1 - \frac{1}{x} + 2e^{-2x} + \cdots$$

Here the polarization would not be proportional to F and it approaches a saturation value. This deviation from propor-

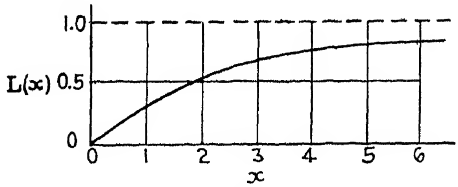

FIG. 54.

tionality occurs only for very high fields, and in experiments especially designed to show this effect. In general, for small values of x one may write with sufficient accuracy

$$L(x) \doteq \frac{x}{3} - \frac{x^3}{45} + \cdots$$

Thus for the weak fields usually used $L(x) = \frac{x}{3}$, and hence

$$\frac{\overline{m}}{\mu} = \frac{1}{3}\frac{\mu F}{KT}.$$

or

$$\overline{m} = \frac{1}{3}\frac{\mu^2 F}{KT}.$$

For electrons or charges which suffer displacement in an electrical field and thus produce a dielectric constant, the Clausius-Mosotti law gave

$$\overline{m} = \gamma F,$$

or

$$\gamma = \frac{\overline{m}}{F},$$

and where the quantity $\nu = \frac{4\pi}{3}$ one had

$$P_0 = \frac{\delta - 1}{\delta + 2}\frac{M}{\rho} = \frac{4\pi}{3}N_A\gamma.$$

If, however, permanent dipoles exist, they alone produce a quantity

$$\frac{\overline{m}}{F} = \frac{1}{3}\frac{\mu^2}{KT}$$

which must be their contribution to the measured polarizability of the molecule. Hence for molecules that have displaceable charges and constant dipoles the γ used before is not just the polarizability γ' due to displacement of charges, but is given by

$$\gamma = \gamma' + \frac{1}{3}\frac{\mu^2}{KT}.$$

Thus, in general, the molecular polarizability P_0 should be written

$$P_0 = \frac{4\pi}{3}N_A\gamma = \frac{4\pi}{3}N_A\left\{\gamma' + \frac{\mu^2}{3KT}\right\} = \frac{\delta - 1}{\delta + 2}\frac{M}{\rho}.$$

Thus P_0 is a function of temperature and so is the measured $\frac{\delta - 1}{\delta + 2}\frac{M}{\rho}$ for all substances for which μ is not 0 (*i.e.*, all polar molecules).

It can be seen at once why $P_0 = \Omega$, the volume of the conducting spherical molecules is so abnormally great for NH_3, HCl, and similar gases. P_0 should be calculated from $\frac{4\pi}{3}N_A\gamma'$, which is the effect of the displacement induced by the field on the molecules considered conducting. But since μ is large for these molecules, the observed δ, which depends on both types of dielectric action, gives values for P_0 that are far too great, and hence values of Ω that do not agree with the real values. If γ' be estimated from the Van der Waals' constants, then the relative importance of dipole and displacement effects can be estimated. Since the high value of μ is due to atomic grouping in certain molecules, it is a specific property of those molecules, and hence it is the appearance of a high μ in some groupings that interferes with the additive law. The Lorenz-Lorentz relation

$$\frac{n^2 - 1}{n^2 + 2}\frac{M}{\rho} = P = \frac{4\pi}{3}N_A\gamma'$$

holds, shows little or no temperature variation and shows additivity because for light the electrical fields alternate so rapidly that the molecules with their high inertias and low frequencies of rotation cannot respond. Thus the contribution to γ by the permanent dipoles is nil and the value of P is governed only by the mobile displaceable electrons which can follow the field. Near a resonance frequency (*i.e.*, absorption band of the substance), the electrons are hampered in their motions, γ' is not given by the Lorenz-Lorentz law, and this theory fails. Thus

one sees how simply and completely the qualitative discrepancies which lead to this investigation are explained. In the next section the quantitative agreement will be given.

97. Experimental Verification of the Debye Theory.—The new expression for the molecular polarizability P_0 is now

$$P_0 = \frac{4\pi}{3} N_A \left(\gamma' + \frac{\mu^2}{3KT}\right).$$

This takes on the form $P_0T = a + bT$, where a has the value

$$a = \frac{4\pi}{3} N_A \frac{\mu^2}{3K},$$

and b the value

$$b = \frac{4\pi}{3} N_A \gamma'.$$

Thus $P_0T = \frac{\delta - 1}{\delta + 2} \frac{M}{\rho} T$ plotted against T gives a straight line, whose intersection with the axis of ordinates evaluates a, and whose slope evaluates b. The results for NH_3 are plotted in Fig. 55.

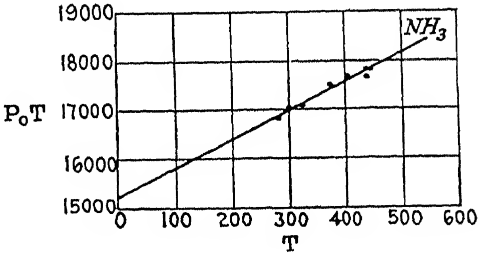

FIG. 55.

As is seen, they lie on a straight line within the limits of accuracy of the measurements. From these results a is found to be 15,250, and b 5.45. Since a has a finite value it must be assumed that NH_3 has a considerable permanent moment. Taking $N_A = 6.06 \times 10^{23}$ and $K = 1.37 \times 10^{-16}$, μ is found to be $\mu = 1.56 \times 10^{-18}$. If the electron is taken as 4.77×10^{-10}, the length of the dipole, that is, the distance between the charges is 3.27×10^{-9} cm, that is, assuming the dipole to be a single positive and negative charge separated by 3×10^{-9} cm one would obtain the value of μ observed. This distance is of the order of magnitude of the distances which atomic charges might be considered to assume between them in a molecule. The idea at once suggests itself that this distance might be equal to that between the nuclei of H and Cl in a gas like HCl. Recently, Zahn[11] has measured a and

b for the three halogen acids, HCl, HBr, and HI. He obtains for μ divided by the electron the three values 0.217, 0.165, and 0.080×10^{-8} cm. According to a recent quantum-theory deduction due to W. Pauli,[12] Jr.,

$$\frac{\delta - 1}{\delta + 2} = \frac{4\pi}{3} N_A\left(\lambda e^2 + 1.5367\frac{\mu^2}{RT}\right).$$

This equation has the same form as that of Debye, which was based on the classical theory above. It differs in the constant factor 1.5367 entering into the doublet or μ^2 term compared to the value $\frac{1}{3}$ of Debye. The values of μ computed by this theory are related to μ from the classical theory in the following fashion.

μ (classical) $= 2.15\ \mu$ (quantum). Thus if the μ calculated on the classical theory from the data gave values of $\frac{\mu}{e}$ greater than the values observed from other measurements, Pauli's theory would be proved to be the more correct. Now band spectra measurements in HCl and HBr make it possible to determine the distance between nuclear centers for these molecules. The values found for this distance are 1.27×10^{-8} and 1.3×10^{-8} cm for these two molecules. The results are thus not adequate to differentiate between the two theories. That the value of $\frac{\mu}{e}$ should be less than the nuclear separation means merely that the interaction of the force fields of the charges in the molecule and their distribution give a dipole whose moment is equivalent to two elementary charges of opposite sign separated by a distance of 0.217×10^{-8} and 0.165×10^{-8} cm, that is, the two charges are not segregated in the centers of the two atoms. How the charges are distributed and how this is related to the nuclear distance is unknown.[13] It is sufficient for the theory that the value of $\frac{\mu}{e}$ is of the order of magnitude of 10^{-8} cm.

The value of b for NH_3 should give a reasonable agreement with the value of P calculated for optical frequencies (where the permanent dipoles do not figure) from the relation

$$P = \frac{n^2 - 1}{n^2 + 2}\frac{M}{\rho}.$$

The agreement should not be perfect, owing to the presence of absorption bands. But extrapolation by means of the Cauchy formula to 0 frequency should yield values of P in rough agree-

ment with b. P from such data comes out 6.13 cm³, compared to the 5.45 observed for b above. This is a satisfactory agreement. From the relative magnitude of $\frac{a}{T}$ and b one can get the relative magnitudes of γ' and $\frac{\mu^2}{3KT}$, the contributions of the displacement dipoles to the polarization. Thus for NH_3, $\frac{a}{T} = 50.8$ and $b = 5.45$. Hence b is about one-tenth of $\frac{a}{T}$ and the polarizability of the NH_3 molecules is due largely to its great permanent dipole moment.

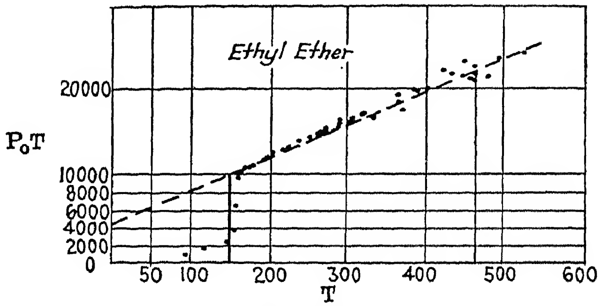

FIG. 56.

These calculations hold unqualifiedly for gases. For liquids this is subject to a restriction. If the molecules with permanent dipoles are completely free to move and have their dipole strength unaltered in the liquid state by combinations, then the law must hold for both. If the liquid is one in which the molecules tend to associate, that is, join in groups of two, three, or more molecules as the temperature changes, then the dipole strength is altered and the law does not apply. Both types of substances exist. Thus in ethyl ether some 50 values of P_0T from solid to gaseous state have been plotted in Fig. 56 as a function of T. From the critical temperature to the neighborhood of the melting point of the solid state T_s they lie on a straight line. Below the melting point they fall down rapidly. A similar change in dielectric constant for water is noted for the melting point. Thus water has a value of $\delta = 88$, while the value for ice is 3.8. This indicates an abrupt change of the dielectric constant on solidifying.

The curve for ether gives $a = 4400$ and $b = 38$. This gives a moment $\mu = 0.84 \times 10^{-18}$. The value of P from optical data is 22.8 in rough agreement with b. The difference is due to the absorption in the infra-red. For ether $\frac{a}{T} = 14.7$ cm³, which is less than one-half the value of b. Hence for this substance the displacement polarizability is more than double the permanent dipole contribution to the polarizability.

Figure 57 gives the curve between P_0T and T for ethyl alcohol, which is a typical associative substance. It is interesting to note that again the points lie closely on a straight line. In this case the slope is such that a takes on a negative value. The five points above 350° lie on a different line. These were obtained from

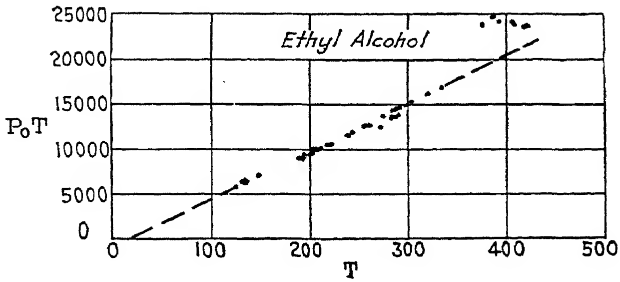

FIG. 57.

observations on the vapor. Could a straight line be drawn through them they would give positive values of a of considerable magnitude, indicating a high value of $\frac{a}{T}$ and a relatively low value of b. Through association in the liquid state as temperature decreases the combinations of molecules annihilate the permanent dipoles. As these constitute most of the dipole strength, the rapid annihilation as association occurs gives the $P_0T - T$ curve a slope in this region, which, if extrapolated to the axis of ordinates, would give a negative value. It is probable that the curve flattens out below 100° abs. and gives a positive value for a corresponding to the solid state. Needless to say, measurements made in such liquids where association is taking place can lead to no values for a and b of any significance.

Below is given a table of the dipole moments (*i.e.*, values of μ) for a number of substances:

Carbon dioxide (CO_2)	0.142×10^{-18}
Carbon monoxide (CO)	0.118
Ammonia (NH_3)	1.53
Sulphur dioxide (SO_2)	1.87
Methyl alcohol (CH_3OH)	1.61
Water (H_2O)	1.87
Hydrochloric acid (HCl)	2.15
*Hydrochloric acid (HCl)	1.034
*Hydrobromic acid (HBr)	0.788
*Hydriodic acid (HI)	0.382
*Sulphur dioxide (SO_2)	1.62
*Ammonia (NH_3)	1.44
*Carbon dioxide (CO_2)	0.06
Ethyl ether ($C_2H_5OC_2H_5$)	0.84
Methyl alcohol (CH_3OH)	1.64
Propyl alcohol (C_3H_7OH)	1.66
Nitrobenzol ($C_6H_5NO_2$)	3.75
Acetone (CH_3 $COCH_3$)	2.61

* Recent measurements due to Zahn. (See K. T. Compton,[14] *Science*, **63**, 53, 1926.)

The theoretical treatment of the question may be further extended to a study of the polarization in mixtures. Here again two classes of substances can be discerned—those mixtures in which no association takes place and those in which it occurs. The former are typified by ethyl ether-benzol mixtures. These follow the theoretical variation for the polarizability of the mixture which would be deduced from the percentage composition and the polarizability of the two molecular types. A study of the second type of mixture, such as benzol-ethyl alcohol mixtures, leads to very complicated curves. From an analysis of these curves, Debye is able to segregate the part due to the polarizability of the alcohol, and thus obtains a curve which gives the molecular polarization of the alcohol as a function of the concentration. This curve is given in Fig. 58. It is seen that this starts at 0 concentration with a value of 71.7 cm³ for P_0 and then increases. After passing through a maximum of 95 cm³ at 35 per cent it falls off to a value of about 50 at 100 per cent alcohol. The value at infinite dilution is the value for the unassociated single molecule. This is borne out by a measurement of the lowering of the freezing point, which indicates that at

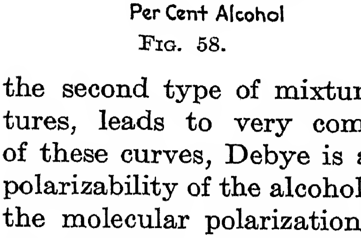

FIG. 58.

great dilutions the molecules are present as single units. Thus the measurement of the value of P_0 for alcohol can be made in dilute solutions. This has been done for other associative liquids also (*e.g.*, methyl alcohol, propyl alcohol, and nitrobenzol in benzol, and methyl alcohol in toluol). For ethyl alcohol the index-of-refraction method applied to the vapor gave a displacement polarization $P = 13.2$ cm³ and the liquid alcohol yielded 12.7 cm³. Taking the mean as 13 cm³, the contribution of the permanent dipoles in this to the total polarizability of 72 for the substance $\frac{a}{T}$ is 59 cm³. Hence the moment μ for ethyl alcohol is $\mu = 1.66 \times 10^{-18}$.

A further study of associative liquids could be made by a measurement and analysis of the molecular polarization of dilute solutions as a function of the temperature. These should yield a variation of P_0T with temperature of the form $a + bT$, and so lead to an evaluation of μ. This has been carried out by one of Debye's pupils. The explanation given by Debye of the form of the curve shown for ethyl alcohol in benzol is instructive. Owing to its high dipole strength, the alcohol molecules tend to join in groups of one, two, and more molecules. This tendency is counteracted by the temperature motion. In great dilutions they are, on the average, unassociated. At high concentrations the chance of association is increased, for, since they are, on the average, nearer together, groups form more often and more are in groups. It now remains to see how an associative substance can first increase its polarization and then decrease it as concentration increases. If two *spherical dipolar* molecules come together, their position of minimum potential energy is with the axes of the dipoles in line, the positive pole of one being near the negative pole of the other. The moment of such a configuration is twice the moment of a single dipole. For three such molecules the axes orient themselves in such a way that they lie along the sides of an equilateral triangle, each positive pole being towards the nearest negative pole. Such a configuration will have a resulting moment of 0. Thus the first stage of association has a moment double that of a single molecule, the second stage one which is 0. With this picture, if one add alcohol to pure benzol in increasing concentrations, at first one should get a formation of double molecules, that is, if this association were complete, one would have, instead of N_A molecules of moment μ and contribut-

ing to the molecular polarization a factor $N_A\mu^2$, $\frac{N_A}{2}$ molecules of moment 2μ which contribute to the molecular polarization a factor of $\frac{N_A}{2}4\mu^2$, that is, twice the original factor. Thus as long as the number of association groups of this type increases the molecular polarization increases. As association progresses with increasing concentration, groups of the type of three molecules of zero moment will form. These contribute 0. As the number of these groups increases relatively to the bimolecular groups, the molecular polarization must drop rapidly. In practice, it is doubtful whether all groups take on the positions of minimum potential energy; but even approximation to this will explain all the phenomena observed in this case. In nitrobenzol the polarization P_0 is 335 cm³, while the value from the index of refraction $P = 33$ cm³. This leads to a moment μ of value 3.75×10^{-18}. Such a molecule should show a marked association. This is the case for nitrobenzol, but in this case the molecular polarization does not increase at first as concentration increases, as was the case for alcohol. In fact, it decreases rapidly at first and more slowly later. The explanation of this would require a different model. Here the molecules would have to be ellipsoids of revolution with the minute dipoles parallel to the major axes at the center. In this case the molecules would associate by bringing the minor axes in contact and so have in the bimolecular state zero moment. It is obvious that such a picture is purely speculative, and it can be fruitful only in that it suggests further experiments.

Debye has also considered the case of electrical oscillations whose frequency lies between the infinitely slow oscillations giving P_0 and the rapid light vibrations giving P. In this region the time is long enough so that the alternating field changes sufficiently slowly to react on the permanent dipoles to an appreciable extent. Under these conditions the polarization will depend on the relation of the period of relaxation (*i.e.*, the time required for the molecular dipole to respond to the field) to the period of the alternating field. This must, in part, depend on the coefficient of viscosity of the surrounding liquid and on the size of the molecule. By an analysis using the law of equipartition and statistical relations similar to the treatment of Brownian motions, he arrives at a definition of the time of

relaxation $\frac{1}{\omega_0} = \frac{8\eta a^3}{2KT}$, which is a characteristic of the particular substance, and determines its behavior. Assuming values for the constants for water, he computes that for values of $\omega_0 = 32 \times 10^{10}$ to 4×10^{10}, that is, for oscillations of wave length from 0.58 to 4.6 cm, water should begin to show the effect of its permanent dipoles in the value of P. The values of P are calculated on this basis, but the calculations are beyond the scope of this text. The values are complicated by absorption of energy in this region and their study properly belongs in the field of anomalous dispersion in light. According to Rubens the calculations are in agreement with experimental facts.

II. APPLICATION OF THE KINETIC THEORY OF THE MAGNETIC PROBLEM

98. Introduction.—In general, two types of magnetic action are recognized. These two types are exemplified by the classes of substances denoted as diamagnetic and paramagnetic substances, respectively. It is asserted, and generally believed, that the diamagnetic behavior is common to all substances, including the paramagnetic bodies, but that in the latter case the paramagnetic behavior where it exists is so much more powerful that it masks the diamagnetic behavior. The diamagnetic bodies can be characterized by two tendencies, both ascribable to the same action, that is, substances like Bi and Cu when placed in a strongly divergent magnetic field are repelled by the pole. Also when a rectangular piece or a piece of one of these metals having a greater length along one axis than another is suspended in a uniform magnetic field, the piece sets itself so that the long axis is at right angles to the magnetic field. These tendencies are real but on the whole relatively weak. The paramagnetic bodies, on the other hand, show just the opposite behavior, that is, they are attracted to the poles in a strongly divergent field and set themselves with their long axes parallel to a uniform magnetic field.

In terms of a picture of the magnetic field represented by Faraday lines of force, the diamagnetic behavior could be described by assuming that the diamagnetic bodies have *less* lines of force running through them than normally would exist in the space occupied by them, that is, they have a permeability less than unity which is ascribed to free space. For the paramagnetic

behavior the tendency is to have a *greater* number of lines of force running through them than would pass through the empty space which they occupy, that is, they have a permeability greater than unity, the value for free space. For the *ferromagnetic* substances this increase in the lines of force is a very large number of times greater than unity, while for the diamagnetic case the reduction in permeability is not much below the value for free space. As will be seen later, the ferromagnetism is merely a type of behavior exhibited by paramagnetic bodies in the proper temperature range. Paramagnetic phenomena have been ascribed to the existence in substances of small permanent molecular magnets, or molecular magnetic dipoles which can orient themselves in a magnetic field, so that their axes tend to correspond with the directions of the field, their north poles being oriented to the south pole of the field. Such an action would be counteracted by the disorienting heat motions of the molecules. Thus it would be expected that the permeability would decrease as temperature increased, and the paramagnetic properties would markedly depend on temperature. In this state they act as if the substance which they compose had become a magnet whose lines of force must be added to that of the inducing field, and, in fact, the quantities defining the effect of a field on a paramagnetic substance have, in part, been formulated from this viewpoint. To account for diamagnetism, it would be necessary, on a similar viewpoint, to assume that such a substance brought into a magnetic field had a magnetic field induced in the molecules present that opposed the existing field, and so reduced the number of lines of force passing through the body. That is, one would have to suppose that the molecules of Bi when brought into a field became magnets whose north poles were directed towards the north pole of the field.

An action of this type could at once be accounted for on the basis of Lenz's law of magnetic induction. If the molecules were of such a nature that they contained small *resistanceless* closed electric circuits, they would, when placed in a magnetic field, have currents induced in them, which, according to Lenz's law, would set up magnetic fields opposed to the acting magnetic field. Owing to the lack of resistance, these currents, and hence the field, would persist as long as the external field acted. In removing the external field, currents in the reverse sense and of equal magnitude would be set up, and when the field was gone there would be no resulting magnetism in the molecules or atoms.

action would manifestly be independent of temperature, isorientations of the molecules due to heat in the mag- d would merely serve to annihilate the fields of some of cules while creating new field in others, since the orienta- he current circuits in the external field would be the ing action. This is found to be the case.

.e Explanation of Diamagnetism.—The existence of such eless circuits in the atoms and molecules seemed at first sonable hypothesis. The study of atomic structure in ars has, however, definitely indicated that this must be The existence of the electron, and the fact that it ι orbit about a central charged nucleus, must lead to just assumption. That the orbits in which the electrons out the nucleus are relatively few in number, governed n energy and momentum relations, and that the radia- loss of energy) of the electrons in these orbits is zero are amental assumptions of Bohr[15] which have led to the le understanding of the atom in relation to spectra now ;. Thus an electron moving in a non-radiating (hence ss) orbit about the nucleus constitutes one of the hypo- esistanceless electrical circuits.

qualitatively, one may regard the effect of the intro- f such a molecule into the magnetic field in the following The electron moving in the orbit has a certain angular and hence possesses a mechanical moment of momen- onsider such a mechanical system oriented in any fashion ırd to the field. It can then be regarded as a small ɜ, the vector representing the moment of momentum mal to the plane of the orbit. If, now, a magnetic field ;ed, it will act on the electron so as to produce a mechan- for the electron in motion constitutes a current which is by a magnetic field. Such an electron is pictured in he nucleus being at N, the electron at E moving in its O marks the vector representing the moment of momen- the particular case in question the force on the electron mponents of the motion perpendicular to the field and ɔ the plane of the orbit will be in a direction such as to rque on the orbit, causing it to tend to rotate about an normal to the field and in the plane of the orbit. For onents of the orbit normal to the plane of the orbit and the field, the resultant forces, will act so as to counter-

balance each other and will produce no effect. On a rotating gyrostatic system the torque exerted on the plane of the orbit results in a precessional motion about an axis normal to the momentum vector NO and to the axis ANB about which the torque exists, that is, the gyrostat will undergo a precessional motion in the direction OP. Thus the electronic gyrostat will, as a whole, move so that the electron rotates in a plane which has a component normal to the direction of the inducing field. But by Lenz's law the sense of this motion must always be such as to cause a field to be created in a direction opposed to the change in the flux through the circuit, so that, on putting on the field, the precession will be such that the magnetic field produced by

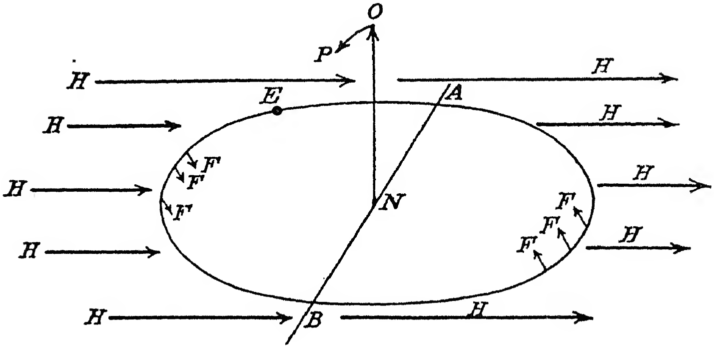

FIG. 59.

the electron of the orbit in its precessional motion will oppose the applied field, that is, the north pole of this precessional magnet will point towards the north pole of the inducing field. On removing the field, the precession will cease and the induced field will disappear. The torque on the electron, and the velocity of precession, and hence the strength of the induced or diamagnetic field, will be proportional to the inducing field. This will hold for all the i electrons in the atom or molecules.

Through analysis which properly does not belong in this text, it can be shown that the magnetic polarizability γ is given by an expression

$$\gamma = -\frac{e^2}{6m_1c^2}\sum \bar{r}_i^{\,2},$$

where e is the electron, m_1 its mass, c the velocity of light, and r_i the average distance of the ith electron path from the nucleus. Now the mass susceptibility χ is given by $\chi = \frac{K}{\rho}$, where K is the mag-

netic volume susceptibility and ρ the density. For these considerations and those that follow the complicating correction for the inner magnetic field may be neglected, since the diamagnetic effects are so feeble as to make this unnecessary. But in analogy to the electrical case in Sec. 96, one may write P, the polarization for unit mass as given by $P = \rho Zm$, where Z is the number of molecules per gram mass, m is the moment induced (which must be γH, where γ is the molecular polarizability, and H is the magnetic field strength). Thus, as

$$P = KH = \rho Zm = \rho Z\gamma H,$$
$$K = \rho Z\gamma \text{ and } \chi = Z\gamma.$$

Hence

$$\chi = -\frac{Ze^2}{6m_1c^2}\sum \bar{r}_i^2.$$

For a gram atom χ_A, the mass susceptibility, will be

$$\chi_A = +A\chi = -\frac{N_Ae^2}{6m_1c^2}\sum \bar{r}_i^2 = -2.85 \times 10^{10} \sum \bar{r}_i^2,$$

where A is the atomic weight and $AZ = N_A$. Now $\sum \bar{r}_i^2$ is the sum of the squares of the average values of the displacements of all electrons from the nucleus, so that dividing $\sum \bar{r}^2$ by "Z," the number of the electrons in the atom (the so-called atomic number), one has a value for $\bar{r}^2$, the square of the average distance of the electron from the nucleus. A few values of $\sum \frac{\bar{r}_i^2}{\text{“}Z\text{”}}$ computed from χ_A are given in the table below. As is seen, the values are, on the whole, close to 10^{-16} cm^2, which is the order of magnitude of the square of the atomic radii, or, better, of the order of magnitude of the orbits of the electrons in the atoms

	"Z"	$-\chi_A$	$\sum \frac{\bar{r}_i^2}{\text{“}Z\text{”}}$
H	1	2.7×10^{-6}	0.95×10^{-16}
He	2	2.2×10^{-6}	0.39×10^{-16}
C	6	6.6×10^{-6}	0.38×10^{-16}
Cl	17	22.0×10^{-6}	0.45×10^{-16}
Br	35	33×10^{-6}	0.33×10^{-16}
Y	53	49×10^{-6}	0.32×10^{-16}
Hg	80	36×10^{-6}	0.16×10^{-16}
Bi	83	280×10^{-6}	1.2×10^{-16}

deduced from the Bohr theory and spectroscopic data. The explanation of the effect, by leading to an agreement of $\bar{r}_i^2$ as deduced from diamagnetic susceptibilities with the accepted values from other data, indicates the correctness of the explanation of diamagnetic phenomenon.

Since the diamagnetic property is dependent on the electronic behavior on the inside of the atom, independence of temperature can be expected. Thus γ, and hence χ, should be found to be independent of temperature. Curie concluded that this was true from his experiments. Later experiments of Honda[16] and Owen[17] showed that this was not strictly true. The elements P, S, and Se show values of χ independent of temperature, while χ in Bi decreases as temperature increases, suffering a very abrupt change at the melting point. Again, it might seem as if the intrinsically atomic nature of the diamagnetic effect should lead to an additive value of γ for different atoms which combine to form molecules. Strange to say, this is, in general (with some exceptions), found to be true, for further reflection reveals that a complex molecule composed of several massive nuclei will not undergo the simple rotation as a whole on application of magnetic field that one would expect in a single atom. For the following elements, then,

	χ_A
H	2.93×10^{-6}
C	6.00×10^{-6}
O	4.61×10^{-6}
Cl	20.1×10^{-6}

From this χ_A can be calculated for $H_2O = -10.5 \times 10^{-6}$, while the observed value is -12.9×10^{-6}. Again ethyl alcohol gives χ_A as -34.2×10^{-6} on computation, and the observed value is -30.5×10^{-6}. Since the orbits of outer electrons are changed by chemical combination, it is surprising that the additivity is as good as it seems to be. There are cases, such as in oxygen, where the atom in combination has its approximate diamagnetic susceptibility, while in some compounds, as in O_2, it is paramagnetic. On the other hand, it must be remembered that, besides the outermost valency electrons which are few in number, the orbits of most of the electrons are little affected by combination, so that χ_A could, on the whole, give a nearly constant average value in combination. The striking feature of this induced magnetism is that it fulfils much the same laws as

does the induced dielectric polarization due to displaced electrons. The treatment of paramagnetism will show that this, in turn, acts analogously to the polarization produced in substances due to the existence of permanent dipoles.

100. Paramagnetic Phenomena in Their Relation to the Kinetic Theory.—As was stated in the introduction (Sec. 98), para- and ferromagnetism were early explained on the assumption of fixed molecular dipoles in the solids whose axes could be oriented by an imposed field. The diamagnetic action described in Sec. 99 must be present in all molecules, but must be completely masked, because of its small value, by the tremendous ferromagnetic effects. The term "paramagnetism" applies properly to all substances whose susceptibilities have a positive value, while the term "ferromagnetic" applies to a special type of paramagnetic action obtaining in some substances below a critical temperature. It is characterized by a very high susceptibility and an enormous inner field.

As far back as 1895 Curie,[18] who had been studying the magnetic behavior of substances, published a paper in which he concluded that for oxygen gas the paramagnetic susceptibility χ per unit mass was inversely proportional to the absolute temperature. Similar experiments on palladium and on ferromagnetic bodies that had lost their ferromagnetism at high temperatures confirmed him in his belief that these were to be explained on the basis of some common kinetic hypothesis. In the general phenomena of magnetism, Curie furthermore saw many analogies to the gas laws. In this he was supported by similar views expressed as early as 1865–1868 by G. Wiedemann. The latter had found that the paramagnetic susceptibilities of solutions of different salts had a temperature coefficient of about the same value as that of an ideal gas. (He found this to be 0.0036 and Plessner later found 0.00355, while the true value for gases at this temperature is 0.00325.) This means, of course, the same thing that Curie found for oxygen, to wit that

$$\chi = \frac{C}{T},$$

where C is a constant and T the absolute temperature. Curie's work led Langevin[19] to derive the expression for the temperature susceptibility of gases on the basis of the kinetic theory. The treatment which he used is identical with the treatment given in

Sec. 96 for the electrical polarization produced in a gas by the presence of permanent electrical dipoles, for Langevin assumed that the paramagnetic susceptibility was due to the existence of small permanent molecular magnets in each gas molecule. These were constantly being disoriented in a superposed field by the heat motions of the molecules. The only change to be made in the treatment for the magnetic case is that now the moment μ is the value of the moment of the permanent *magnetic* moment in the molecule, the acting field is to be the *magnetic field* H instead of the electric field, and the average moment $\bar{m}$ is the average *magnetic* moment of the molecule. It follows at once that if, as the general distribution law demands the number of molecules having moments represented by vectors lying in a small volume element $d\Omega$ is given by $Ae^{\frac{\mu H}{KT}\cos\theta}\,d\Omega$, where θ is the angle of the dipole with the field, then the average moment for a large number of molecules may be written as

$$\bar{m} = \frac{\int_0^\pi e^{\frac{\mu H}{KT}\cos\theta}\,\mu\cos\theta d\Omega}{\int_0^\pi e^{\frac{\mu H}{KT}\cos\theta}\,d\Omega}.$$

(See Sec. 96 of Part I, Chap. X.)
The solution of this yields

$$\frac{\bar{m}}{\mu} = \cot\frac{\mu H}{KT} - \frac{KT}{\mu H} = L\left(\frac{\mu H}{KT}\right),$$

where L stands for the Langevin function. Experimentally for paramagnetic substances, the fields H are always so weak that $\frac{\mu H}{KT}$ is small compared to unity. Thus the approximation given before can be used, namely,

$$L\left(\frac{\mu H}{KT}\right) = \frac{\mu H}{3KT} - \frac{1}{45}\left(\frac{\mu H}{KT}\right)^3 + \frac{\left(\frac{\mu H}{KT}\right)^5}{3780} + \cdots$$

and therefore that, to a good degree of approximation,

$$\bar{m} = \frac{\mu^2 H}{3KT}.$$

For the sake of simplicity, in what follows it may be assumed that the inducing field H is the same as the inner field. This could not be done in the case of dielectrics, as, on the whole, the contri-

bution of the other molecules to the field was considerable. As will be seen later, the magnetic polarization in paramagnetic substances is so feeble that the fields differ by less than one part in a thousand. One may, accordingly, write that as $KH = \rho z\bar{m}$, and $\chi = \frac{K}{\rho}$ (see Sec. 99), therefore

$$\chi = \frac{z}{H}\bar{m} = \frac{z\mu^2}{3KT},$$

where z is the number of molecules per gram. This is Curie's law deduced from theoretical considerations and it is seen that, in fact, χ is proportional to $\frac{1}{T}$, and that the constant C found experimentally by Curie has now a meaning in terms of the molecular magnetic moments, the Loschmidt's number, and the Boltzmann constant. Curie found $\chi = \frac{3.37 \times 10^{-2}}{T}$ in O_2. If this value is accepted, then, as $K = 1.371 \times 10^{-16}$ and $N_A = 1.894 \times 10^{23}$, μ is given by

$$\mu = \sqrt{\frac{3KC}{z}} = 0.856 \times 10^{-20}.$$

To check this value against other quantities, if it is assumed that the moment is caused by the rotation of an electron in an orbit of 0.5×10^{-8}-cm radius, the angular velocity required to give μ above is 4.3×10^{16} radians per second. This is of the order of magnitude to be expected on the basis of earlier optical investigations. The exact relation between paramagnetic behavior and the electron theory has, however, been insufficiently worked out theoretically to make a real estimate of the paramagnetic moments from other data.

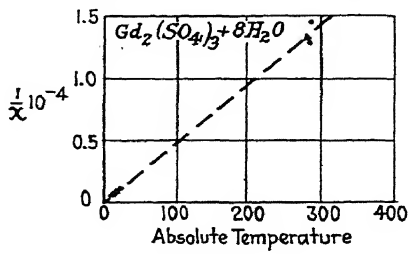

FIG. 60.

The extent to which the Curie-Langevin law is obeyed experimentally may be seen in Figs. 60 and 61 for gadolinium sulphate and oxygen, where $\frac{1}{\chi} \times 10^{-4}$ is plotted against T, the absolute temperature. These two sets of observations follow the Curie-Langevin law quite well, as they are straight lines passing through the origin. Others do not obey it so well.

Langevin's theoretical equation extends to fields, or conditions of field and temperature, such that $\frac{\mu H}{KT}$ approaches unity. Under these conditions, the curve should approach a saturation value, as was shown by the approximation formula to the Langevin function $L(x)$ for this case, to wit

$$L\left(\frac{\mu H}{KT}\right) = 1 - \frac{KT}{\mu H} + 2e^{-2\frac{\mu H}{KT}} + \ . \ . \ . \quad \text{(See Sec. 96).}$$

It was found to be impossible to test this for the dielectric case, as the fields were too weak. In the magnetic case the test of this law is possible. If μ is 10^{-20}, $\frac{\mu H}{KT}$ will become unity when

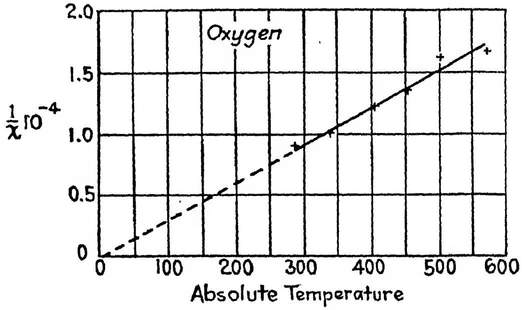

FIG. 61.

$\frac{H}{T} = 1.37 \times 10^4$. Such an effect will have to be tested for at very low temperatures, as fields of 30,000 gausses are already hard to achieve conveniently. Such low temperatures, where the law of equipartition has begun to break down, would make it seem unlikely that the Langevin equation based on it would be applicable. Kammerlingh-Onnes in 1914 found that ($Gd_2(SO_4)_3 8H_2O$) at 1.9 and 4.25° abs. had a magnetization which was not proportional to the field H applied, while at 20.3° abs. the magnetization was strictly proportional to the field. This substance was chosen for three reasons: It follows the Curie law down to 20° abs. With its eight molecules of water of crystallization it can be regarded as a dilute solution. Finally, it has a very high value for μ ($\mu = 7.2 \times 10^{-20}$). The result of later measurements by Kammerlingh-Onnes and H. R. Woltjer[20] are shown in Fig. 62

where $\frac{\overline{m}}{\mu}$ as ordinates are plotted against $\frac{\mu H}{KT}$ as abscissæ. If the Langevin law holds, the points should lie on a curve

$$\frac{\overline{m}}{\mu} = \cot \frac{\mu H}{KT} - \frac{KT}{\mu H}.$$

The figure shows that the points fall closely onto the smooth curve calculated by the above formula. The upper points corresponding to an $\frac{\overline{m}}{\mu}$, which is 84 per cent of the saturation value, were taken at 1.31° abs., in a field of 22,000 gausses. Considering the fact that, theoretically, these experiments were made on solids where free rotations were restricted, and at temperatures where

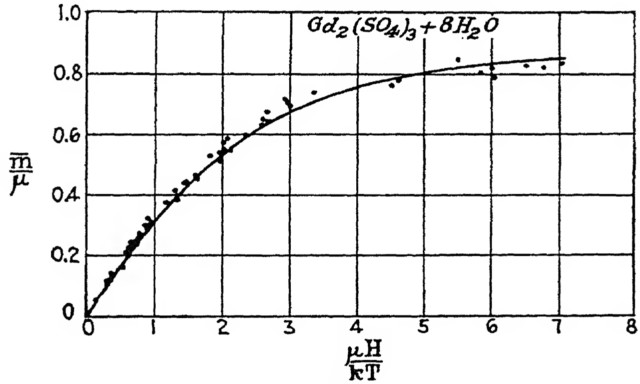

FIG. 62.

the assumptions underlying the theory are very doubtful, the agreement is surprisingly good.

101. The Inner Field and Its Application to Ferromagnetism.— In the last section it was assumed that the force acting to orient the molecular dipoles was H, the impressed field. In Sec. 96, on dielectric constants it was seen that the field is not the impressed field, but the so-called inner field of the substance, that is, the polarization is not proportional to H, the impressed field, but to H', the inner field, where H' is given by

$$H' = H + \nu P.$$

Here P is the intensity of magnetization, or what was termed, in analogy to the electrical term, the magnetic polarization. ν is the proportionality factor (the constant of the inner field) which was a pure number and for either a regular molecular lattice or

for a perfectly random distribution of molecules took the value $\frac{4\pi}{3}$. For oxygen or cases similar to those used in the preceding section, P was small. Thus for oxygen at 273° abs. compressed to the same density as water, the value of C is $= 3.37 \times 10^{-2}$ from Curie's observations. This would give P the value $1.23 \times 10^{-4}H$. For a value of $\nu = \frac{4\pi}{3}$ this makes $H' = 1.00051H$, that is, it adds an entirely negligible correction. A similar consideration for $Gd_2(SO_4)_3$ at the lowest temperatures leads to a correction of $\frac{4\pi}{3} P = 0.195H$. This correction is considerable and indicates that under some conditions ν cannot be neglected at low temperatures. While the action shown by O_2 holds for many substances, it does not exclude the possibility of the orientation of the molecules by the field being accompanied by other changes which could influence ν very markedly. With changes in ν, the whole treatment must be changed. To this end P. Weiss, to whom the following treatment was due originally, left ν undetermined and carried out the discussion of what the effect of ν would be by an analysis of the resulting equations. The study of these considerations and the applications to experiments will now briefly be given. They lead to a definition of ferromagnetism.

Call $H' = H + \nu P$.

According to Langevin, it was found that

$$\frac{\bar{m}}{\mu} = L(x) = \cot x - \frac{1}{x},$$

where $x = \frac{\mu H'}{KT}$. Call $P = \rho z \bar{m} = \rho z \mu \frac{\bar{m}}{\mu}$, where ρ is the density of the substance and z the number of molecules in a gram. Thus

$$\frac{KTx}{\mu} = H + \nu z \rho \mu \frac{\bar{m}}{\mu}, \text{ and}$$

$$\frac{\bar{m}}{\mu} = \frac{KT}{\nu \rho z \mu^2} x - \frac{H}{\nu \rho z \mu}.$$

One accordingly has $\frac{\bar{m}}{\mu}$ expressed as a function of $\frac{H}{\nu \rho z \mu}$ for a given value of $\frac{KT}{\nu z \rho \mu^2}$, when x is found. Graphically, this may

be represented as in Fig. 63. The expression of $\frac{\bar{m}}{\mu} = L(x)$ is plotted as ordinates against x as abscissæ. On the same diagram the value of $\frac{\bar{m}}{\mu}$ is plotted as ordinate against x in terms of the equation

$$\frac{\bar{m}}{\mu} = \frac{KT}{\nu\rho z\mu^2}x - \frac{H}{\rho\nu z\mu}.$$

For the case where $H = 0$, there is a straight line AOB passing through the origin O. For positive values of H the latter curve lies below the $H = 0$ curve. It is a straight line cutting the axis of ordinates at O' below the origin O. This at once shows

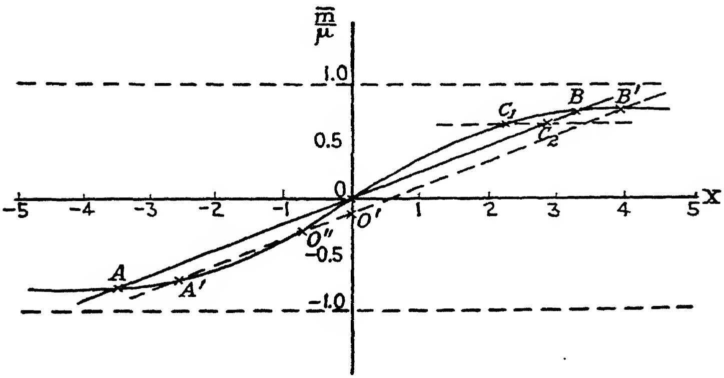

Fig. 63.

that two possible cases may occur: For the case where $H = 0$, the straight line for small values of $\frac{KT}{\nu\rho z\mu^2}$ will cut $L(x)$ in three points, O, B, and A. For large values of $\frac{KT}{\nu\rho z\mu^2}$ the straight line for $H = 0$ will cut the curve $L(x)$ only in one point O. In the latter case $\left(\text{that is, for } \frac{KT}{\nu\rho z\mu^2} \text{ having large values}\right)$, for $H = 0$ one also has $x = 0$ and $\frac{\bar{m}}{\mu} = 0$, that is magnetization can only be called forth by an external field H.

For a field H which is not too great, the point of intersection for finite values of H will lie in the neighborhood of the origin, that is, one will be far removed from conditions of saturation and one

can replace $L(x)$ by its low value of x approximation, to wit $L(x) = \frac{x}{3}$. This leads at once to a simple solution for the equations above, and

$$\frac{\bar{m}}{\mu} = \frac{x}{3} \text{ and } \frac{\bar{m}}{\mu} = \frac{KT}{\nu\rho z\mu^2}\,x - \frac{H}{\nu\rho z\mu}.$$

These yield at once

$$\frac{\bar{m}}{\mu} = \frac{\mu H}{3K}\,\frac{1}{T - \frac{\nu\rho z\mu^2}{3K}}.$$

This may be compared with the expression for a negligible ν

$$\frac{\bar{m}}{\mu} = \frac{\mu H}{3KT}$$

and one sees at once it differs by the factor $\frac{1}{\left(1 - \frac{\nu\rho z\mu^2}{3KT}\right)}$ from the simple case for $\nu = 0$. As ν is a pure number, the quantity $\frac{\nu\rho z\mu^2}{3K}$ can be looked on as a temperature Θ, for it has those dimensions. Thus one can regard $\Theta = \frac{\nu\rho z\mu^2}{3K}$ as a critical temperature for which $\bar{m}$ becomes theoretically infinitely great. Thus if

$$\frac{\bar{m}}{\mu} = \frac{\mu H}{3K}\,\frac{1}{(T - \Theta)},$$

when $T = \Theta$, $(T - \Theta) = 0$, and $\frac{\bar{m}}{\mu}$ is infinite. The Curie law giving the susceptibility per unit mass as $\chi = \frac{C}{T}$, where $C = \frac{z\mu^2}{3K}$, when the action of the inner field is included, becomes

$$\chi = \frac{C}{T - \Theta}.$$

This equation is called the Weiss law after its discoverer Pierre Weiss. Since $C = \frac{\Theta}{\nu\rho}$ this law may be written as

$$\chi = \frac{1}{\nu\rho}\,\frac{\Theta}{T - \Theta}.$$

For the case that the temperature T is lower than the critical temperature Θ, the equations may be simplified by using Θ. They then read

$$\frac{\bar{m}}{\mu} = L(x),$$

$$\frac{\bar{m}}{\mu} = \frac{T}{\Theta}\frac{x}{3} - \frac{\mu H}{3K\Theta}.$$

If $\frac{T}{\Theta}$ is less than unity, the slope of the curve is less than the initial slope of the $L(x)$ curve. This means that even for $H = 0$ the straight line cuts the $L(x)$ curve in three points. It can be demonstrated that the intersection at B is a stable point while the one at O is unstable. Thus magnetization at B occurs for $H = 0$, that is, it is a spontaneous magnetization, and the value of the average moment produced will be designated by m_s. Accordingly,

$$\frac{\bar{m}_s}{\mu} = L(x),$$

and

$$\frac{T}{\Theta} = 3\frac{L(x)}{x} \text{ as } H = 0.$$

There is, accordingly, in paramagnetic substances the following condition: Above a critical temperature Θ all substances are paramagnetic. Below this they are spontaneously magnetized and possess the properties which Weiss identifies with the ferromagnetic state. The critical temperatures for a number of substances are given in the table below:

Substance	Θ
Fe	758 + 273
Ni	374 + 273
Co	1137 + 273
FeNi	365 + 273
Magnetite	585 + 273
Pyrrhotine	348 + 273
MnP	26 + 273
MnAs	45 + 273

These values are from actual observations of the disappearance of ferromagnetism in these substances. The values as observed by various workers are not, however, closely the same, although they show general agreement. Weiss explains the fact that a piece of iron below 758°C. does not show spontaneous magnetization as being due to the fact that the elementary magnets which exist are not oriented in the metal. In a relatively weak field, however, orientation takes place, so that their axes are parallel and one has the ferromagnetic properties displayed. Saturation

in this case is, however, only relative even when the elementary magnets are parallel, as the value of the moment obtained is determined by the value of the spontaneous magnetization, which is a function of T. The maximum saturation will then appear as only partially obtained, even when the elements are parallel, as, with fields which can be realized, the assistance given to the spontaneous magnetization when $H = 0$ is not enough to raise the value of the magnetization to a higher level. Strictly, this cannot occur, and particularly near the Curie point (that is, the critical point) the molecular field is sufficiently weakened by heat motions so that the ordinary fields used can materially change the spontaneous magnetization. This fact is supported by the magnetocaloric effects, to which reference only may be made. The situation results in a gradual change from the paramagnetic to the ferromagnetic state, instead of the abrupt change which would be expected from the Weiss law, where χ becomes infinite when $T = \Theta$. In fact, it is only for appreciable values of $T - \Theta$ that the linear conditions demanded by the Weiss law are fulfilled. How the spontaneous magnetization and the great intensity (and hence the great increase in χ) can be caused will be seen later. In fact, near Θ the law so changes that near the Curie point a moment is found which is proportional to $H^{1/3}$. Thus at $T = \Theta$, susceptibility in the usual sense does not exist. This law of a moment proportional to the cube root of H forms the transition between the paramagnetic and the spontaneously generated field states, and even the latter state can be influenced rather easily by the field near this point.

To visualize the conditions near $T = \Theta$ the second term must be used in the approximation to $L(x)$, that is,

$$\frac{\overline{m}}{\mu} = L(x) = \frac{x}{3} - \frac{x^3}{45}, \text{ and}$$

$$\frac{\overline{m}}{\mu} = \frac{T}{\Theta}\frac{x}{3} - \frac{\mu H}{3K\Theta}.$$

From this x may be solved for by an equation of the third degree,

$$\left(\frac{T}{\Theta} - 1\right)\frac{x}{3} + \frac{x^3}{45} = \frac{H}{3K\Theta}.$$

Here $\frac{\overline{m}}{\mu}$ can be found by placing the values of x so obtained in

$$\frac{\overline{m}}{\mu} = \frac{T}{\Theta}\frac{x}{3} - \frac{\mu H}{3K\Theta}.$$

This leads to the evaluation of two limiting cases and one transitional case.

If $T > \Theta$, the x^3 term relative to the x term may be neglected as long as $T - \Theta$ is large. Then

$$x = \frac{\mu H}{K(T - \Theta)},$$

which leads to the original Weiss law.

If $T < \Theta$, while $T - \Theta$ is so large that the field H is negligible in its action, then

$$\left(\frac{T}{\Theta} - 1\right)\frac{x}{3} + \frac{x^3}{45} = 0.$$

The root of importance in this case is

$$x = \sqrt{15\left(1 - \frac{T}{\Theta}\right)},$$

so that one gets $\dfrac{\overline{m}_s}{\mu}$ given by

$$\frac{\overline{m}_s}{\mu} = \sqrt{\frac{5}{3}\left(1 - \frac{T}{\Theta}\right)},$$

that is, the curve for spontaneous magnetization should approach the Curie point with a vertical tangent which is observationally found to hold. The equation above is, however, not applicable to that region.

In the transitional case, $T = \Theta$. The equations become

$$\frac{x^3}{45} = \frac{\mu H}{3K\Theta},$$

so that

$$x = \left(15\frac{\mu H}{K\Theta}\right)^{1/3},$$

whence as a sufficient approximation one has

$$\frac{\overline{m}}{\mu} = \left(\frac{5}{3}\frac{\mu H}{K\Theta}\right)^{1/3},$$

that is, near the Curie point (*i.e.*, the critical temperature Θ), $\dfrac{\overline{m}}{\mu}$ is proportional to $H^{1/3}$.

The experimental agreement with the Weiss theory may briefly be tested for the substances Co, Ni, and Fe. The values of $\dfrac{1}{\chi}$

are plotted as ordinates against the absolute temperature in Fig. 64. The theory says that

$$\chi = \frac{C}{T - \Theta}.$$

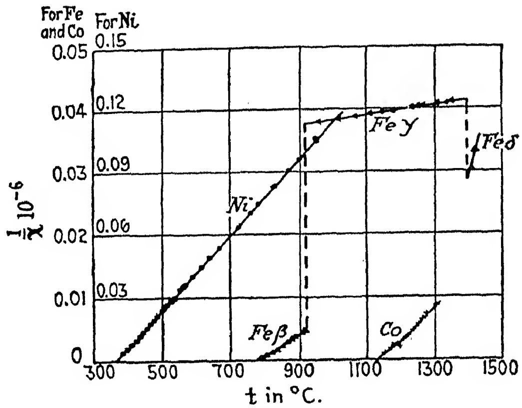

FIG. 64.

Thus the points $\frac{1}{\chi}$ must lie on a straight line which, prolonged to lower temperatures than Θ, must cut the axis of ordinates at $\frac{0 - \Theta}{C}$, and whose slope is $\frac{1}{C}$. As is seen, iron shows three lines of different slopes. They are labeled, respectively, Fe_β, Fe_γ, and Fe_δ. For the critical temperature Weiss finds $\Theta = 774 + 273 = 1047$. Up to $774 + 273$ the curve is given by

$$\chi = \frac{0.0395}{T - 1047}.$$

From $828 + 273$ on to $920 + 273$ the curve has the equation

$$\chi = \frac{0.0273}{T - 1063}.$$

From $920 + 273$ to $1395 + 273$ the equation becomes

$$\chi = \frac{0.072}{T - 1340},$$

and, finally, from $1395 + 273$ on the equation is

$$\chi = \frac{0.0045}{T - 1503}.$$

These four equations represent four magnetic temperature states of iron called, respectively, α, β, γ, and δ iron. The change from α to β iron characterized by the critical temperature (*i.e.*,

the Curie point of 774 + 273) has for some time been known to be the true Weiss transition. Nevertheless, it is still held by some to be due to two different types of iron. X-ray studies have shown, without question, that this is not so and that α and β iron have the same crystal structure. The second change which occurs at 920 + 273 is marked by a change in χ from 210×10^{-6} to $\chi = 28 \times 10^{-6}$. It takes a considerable time to change from one value to the other. It corresponds with Osmond's transition from β to γ iron. This is confirmed by X-ray analysis where the β iron is a space-centered cubical lattice, while the γ is a face-centered cubical lattice. The interesting thing to note is that the Θ is not 1395 + 273, but is -1340, that is, the γ iron has a Θ which is negative. This means a molecular field which opposes the applied field. Such fields are observed in other substances, notably in oxygen. The δ iron transition which occurs at 1395 + 273 has again a normal $\Theta = +1503$ instead of 1668. Curie believed that it could be considered a continuation of the β-type curve. It is interesting to note that the iron in the δ state has actually reverted to a space-centered cubical lattice as shown by X-rays.

For Ni, the curve has no breaks and the equation representing the results is $\chi = \dfrac{0.00555}{T - 645}$, from the Curie point at 357 + 273 to 900 + 273. The equation holds only roughly in the region up to 412 + 273, but after this the agreement is almost striking.

For Co, whose critical temperature is very high, 1131 + 273, the results can be summarized by two intersecting straight lines

$$\chi = \frac{0.0217}{T - 1404}$$

$$\chi = \frac{0.0182}{T - 1422},$$

holding from 1170 + 273 to 1241 + 273, and from 1241 + 273 to 1303 + 273. It seems possible that in this transition, as in α to β iron, one is not dealing with two straight lines but with a single curved line passing through the critical point.

Interesting measurements made in mixtures of liquid oxygen and nitrogen show that the $\dfrac{1}{\chi} - T$ curves are straight parallel lines whose intercepts with the axis of ordinates vary with the composition. This means that the Curie constant C is inde-

pendent of density, while Θ is a function of the density. The Θ for oxygen in this region is negative and is approximately proportional to the density.

The question as to the nature of the inner field which causes the transition is not yet successfully answered. A suggestion of Debye seems to offer a temporary solution, which is, however, quite incomplete.

The value of the inner field ν can be computed from the critical temperature values.

$$\Theta = \frac{C}{\nu\rho}.$$

This leads Weiss to evaluate $\nu = 14{,}000$ for Ni, and 8650 for Co. For the dielectric case as well as for the theoretical magnetic case of disoriented molecules or molecules in a regular crystal lattice, ν was $\frac{4\pi}{3}$ (Sec. 96). These values 10,000 and 4 are not to be compared, and one must look further than the spatial arrangement of molecules alone for a value of ν of the order of 8000 or more. An interesting explanation is offered by the assumption that these substances *have electrical dipoles in their molecules whose orientation is such that their moments lie parallel with the magnetic axes of the magnets.* Thus if a magnetic polarization P_m were to occur, there would be an accompanying electrical polarization P_e. These would be so related in strength that

$$\frac{P_e}{P_m} = \frac{\mu_e}{\mu_m},$$

where μ_e and μ_m are the actual electrical and magnetic moments. Hence on each elementary particle one has the outer magnetic field and the newly oriented electrical field acting simultaneously. The former has the value H if the insignificant contribution $\frac{4\pi}{3}P_m$ is neglected. The electrical inner field has a strength $\frac{4\pi}{3}P_e$ if the Lorentz constant of the inner field is used. The potential energy of an elementary particle then becomes proportional to

$$\mu_m H + \mu_e \frac{4\pi}{3} P_e = \mu_m H + \frac{4\pi}{3}\frac{\mu_e^2}{\mu_m} P_m,$$

that is to say,

$$F = H + \frac{4\pi}{3}\frac{\mu_e^2}{\mu_m^2} P_m.$$

If

$$F = H + \nu P_m,$$

as Weiss put it, then

$$\nu = \frac{4\pi}{3}\frac{\mu_e^2}{\mu_m^2}.$$

This gives values of ν of the correct order of magnitude. The quantity μ_e has the order of magnitude of 10^{-18}, while μ_m has the value of 10^{-20}. This ν is of the order of 100^2, or 10,000, which is the value observed. The theory seems in agreement with certain deductions concerning the law of force between the dipoles. It is also interesting to note that if ν is to be proportional to μ_e^2 positive values of ν must always be expected and hence of Θ. But, as is known, oxygen and γ iron have a negative ν. In this connection, it must be remembered that O_2 has no permanent electrical dipoles as its P and its P_0 are nearly the same (see Sec. 96). Treating oxygen as an electrical quadrupole does not explain the negative ν and it makes the susceptibility too sensitive to temperature changes. The theory, in spite of its unsatisfactory character, leads to further interesting experimental verification, that is, it would be expected that a constant magnetic force would produce a dielectric polarization and a constant electrical force a magnetic polarization if this theory were correct. A. Perrier[21] carried out extensive experiments in this direction. A current was passed down a magnetic conductor and a magnetization resulting from the electrical field was looked for in the direction of the electrical field, that is, the current. The results convinced the workers that the electrical field causes a magnetization acting in the opposite sense. This means that iron atoms must have an electrical moment of $\mu_e = 9.7 \times 10^{-18}$. This is considerably higher than the values estimated for μ_e for iron which comes from the dielectric properties of insulators.

102. The Question of Magnetic Orientation.—The theory of Langevin that underlies the Curie law depends on the assumption that the molecules of the substances, for instance, oxygen, orient themselves in the applied field according to statistical laws. This assumption is perfectly correct for gases and liquids where the molecules are free to turn, and have energy of rotation. It is strange, however, that the application of the Langevin equation to the case of solids, which leads to the Weiss law, should hold for solid paramagnetic bodies, for with these there

is no free mobility of the molecules. In fact, the situation in some crystals leads to serious difficulties. In a large number of paramagnetic crystals the X-ray analysis leads to the undoubted conclusion that the crystal lattice is made up of atoms. For the α, β and δ iron this is a space-centered cubical lattice made up of single atoms. There are, of course, other crystals in which actual molecular groups take positions as single units of the lattice. How molecules of iron in an atomic crystal lattice can rotate it is difficult to see, for the rigidity of the structure prohibits an interchange of positions or a relative displacement of the atoms which could compose any group. This necessitates the assumption that it is the atoms themselves in such a crystal that rotate in a magnetic field. This is possible, but a very serious difficulty is at once encountered. The Langevin equation presupposes rotations in statistical temperature equilibrium. Now, as the chapter on Specific Heats will show, such an assumption is contrary to facts, for atoms do not rotate due to heat motions, as the inert gases and mercury vapor have atomic heats showing only three degrees of freedom and molecular heats of solids roughly follow the Du Long and Petit law where no rotations are included.

In spite of this difficulty, the explanation has been adhered to, with the modification of the theory, to include the quantum theoretical deviations of the energies of rotations of the molecules. Oosterhuis[22] carried this out by replacing the KT of the Langevin theory in $\chi = \frac{z\mu^2}{3KT}$ (which comes from the law of equipartition through giving to each degree of freedom the energy $\frac{1}{2}KT$) by the law that follows from the quantum theory. He based his considerations on the work of Einstein and Stern,[23] who developed a quantum law of partition of energy which gave to the atoms an energy at the absolute 0. The choice of this was made because the low-temperature measurements of susceptibility seemed to show a lower rate of increase than the pure Curie law demanded, thus indicating that at absolute zero there was still an energy of rotation. The energy u of a resonator with a zero point energy $\frac{h\nu}{2}$ is given by quantum theory as

$$u = \frac{h\nu}{e^{\frac{h\nu}{KT}} - 1} + \frac{h\nu}{2}$$

(compare with Sec. 94). The energy ν is to be identified with the energy of rotation of angular velocity ω, so that $\nu = \frac{\omega}{2\pi}$. With this, the energy of a molecule with moment of inertia J is given by

$$u = 2\pi^2 J\nu^2.$$

From this ν may be eliminated and then the susceptibility as developed by Langevin for the case of the Curie law would be found by replacing the KT in that expression by u, thus

$$\chi = \frac{z\mu^2}{3u}.$$

If this is done, development in series for relatively high values of T gives

$$u = KT\left[1 + \frac{1}{12}\left(\frac{h^2}{2\pi JKT}\right) + \dots\right].$$

As a first approximation, this yields

$$\chi = \frac{z\mu^2}{3K}\frac{1}{T + \frac{h^2}{24\pi^2 JK}}.$$

If one calls $\frac{-h^2}{24\pi^2 KJ} = \Theta$, one has at once the Weiss law with a negative Θ which is often found. The measured value of Θ when applied to $\Theta = \frac{-h^2}{24\pi^2 JK}$ further leads to proper values of J for molecules. Thus for anhydrous $MnSO_4$, J comes out 0.87×10^{-40}, for $MnSO_4 \cdot 4H_2O$ it was 11×10^{-40} and for Pt about 0.048×10^{-40}. The increase in the values of J for manganese by the introduction of water of crystallization which increases the moment of inertia also seems a further support. The theory has been further extended by Keesom for ferromagnetic bodies. Nevertheless, as Debye points out, the atomic nature of crystal lattices seems definitely to negative this whole notion of orientation of molecules.

It is thus essential that a theory be devised which does not demand the free rotation. In this direction both Weiss[24] and later Lenz[25] made use of an idea which reduces the rotations in the field to very small ones. In this theory the moments of the elementary magnets are oriented in either one direction or 180 deg. from this, and the probabilities of other orientations are distinctly less, for

they depend on the presence of a potential energy. From this it follows that the Langevin function $L(x) = \cot x - \frac{1}{x}$ must be replaced by another function $Le(x) = \tan x$. This does not solve the problem, as the free rotation is not eliminated but merely reduced. Ehrenfest again altered the Lenz equation with perhaps a slightly more permissible assumption. The results are, however, not satisfying, and serve with Lenz's as merely indicating a way in which to attack the problem. The conclusion to be drawn from this discussion is that, while the Langevin explanation does apply to solutions and gases, *it is not theoretically applicable* to crystals, even though by its aid the apparently correct Weiss equation for crystals and solid substances is derived.

103. The Weiss Magneton and the Bohr Magneton.—The Curie constant C in magnetic phenomena has, through the Langevin equation, the value $C = \frac{z\mu^2}{3K}$. From this it is possible to evaluate μ, the magnetic moment of the molecule. Now C, and thus μ, may be evaluated from measurements on the susceptibilities of solutions or gases, and from the Weiss law $\chi = \frac{C}{T - \Theta}$ for solids. According to Weiss, μ may also be found by measuring the polarization P_0 of the saturation magnetization at absolute zero, where $P_0 = \rho_0 \mu z$. From these values for a large number of substances, one obtains M, the moment of a gram-atom. Such values are given for some substances in the table below.

Substance	M in C.G.S. Units
Ni	3,381
Co	9,650
Fe	12,410
Magnetite	7,417

Using these values, Weiss computes the least common divisor and obtains a value of M of about 1126. This he assumes is *the value of the elementary magnetic moment of an atom or magneton.* Thus, Ni has three, Co about nine, Fe eleven, and magnetite about seven magnetons. In general, he believes this holds for all substances.

The Bohr theory of spectral lines, however, leads to another value. According to this theory, the moment of momentum of an electron in the atom is a whole multiple of the quantity $\frac{h}{2\pi}$,

where h is the Planck constant of quantum action. Now the laws of dynamics give a relation between the moment of momentum i of the electron and the magnetic moment of the molecule of the form

$$\mu = \frac{e}{2mc} i,$$

where e is the electron, m its mass, c the velocity of light, and μ the magnetic moment. Thus for a gram-atom of substance the magnetic moment M' of the magneton is

$$M' = \frac{N_A}{4\pi} \frac{eh}{mc} = 5593,$$

that is, about five times the value found by Weiss.

The relation of the two magnetons was calculated by W. Pauli, Jr.[26], who made use of the action of the magnetic field on the Zeeman effect in altering the moment of momentum of the electron. He further assumed that, besides the quantum changes that occur, for instance, for an atom like hydrogen in a magnetic field, the probability of the appearance of each quantum change is governed by the Boltzmann probability factor $e^{-\frac{u}{KT}}$, where $u = -\mu H \cos\theta$, μ being the moment, H the field strength, and θ the angle. The considerations lead to the relation between m_w, the Weiss magneton, and m_B, the Bohr magneton, embodied in the equation below:

$$p\left(\frac{m_w}{m_B}\right) = n\sqrt{3 \overline{\cos^2 \theta_i}} = \sqrt{(n+i)\left(n+\frac{1}{2}\right)}.$$

Here p is the number of Weiss magnetons and is obtained from $C = \frac{p^2}{3} \frac{zm_w{}^2}{K}$, C being the Curie constant and m_w the Weiss magneton. $\overline{\text{Cos } \theta_i}$ is the average value of the cosine of the angle, m_B is the Bohr magneton, and n is the quantum number of the orbit considered. If $\frac{m_w}{m_B} = \frac{1126}{5593}$, one has

$$p = 4.967\sqrt{(n+1)\left(n+\frac{1}{2}\right)}.$$

If $n = 1, 2,$ etc. the values of p are:

n	1	2	3	4	5
p	8.6	13.6	18.6	23.6	28.5

For NO and O_2, Pauli compares the observed values 9.18 and 14.13 with the computed value of p for the first two values of n. These differences are, according to Weiss, greater than those to be ascribed to experimental error, so that the Pauli theory is not successfully established. The theory of Pauli was later extended by Sommerfeld.[27] The values he obtains are not materially different from those of Pauli, so that the discrepancies are still outstanding.

The reality of the Bohr magneton has been definitely proved by the recent experiments of Stern and Gerlach,[28] who have shown the quantization of the orientation of the magnetic moments of silver atoms. The arrangement is simple. An

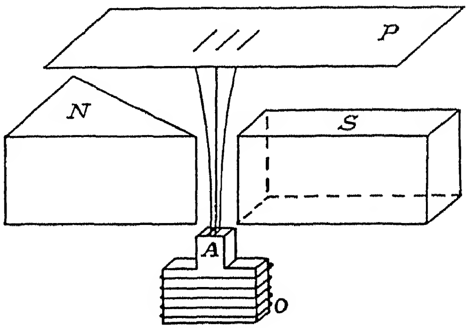

FIG. 65.

atomic stream of silver atoms from a slit S in an oven O (Fig. 65) passed through the strongly divergent field of a magnet pole N in a high vacuum. They then fell on a plate of glass P. Now monatomic silver atoms have one electron (the valence electron) in a single quantum orbit. From the quantum theory this should lead to the possibility of only two orientations of the Ag atom in the field. Its axis must be in the direction of the field with either the north pole towards the south pole of the field or 180 deg. from this, with the south pole towards the south pole of the magnet. It is well known that in a divergent field a magnet of magnetic moment m_x will experience a force urging it to or from the magnet pole depending on whether its north pole is towards or away from the south pole of the magnet. Thus the beam of silver atoms which gives a single line image in the absence of the field should be split into two distinct lines separated by an amount depending on the field, when the field is applied. This is just what was observed. Thus the quantization of the magnetic moments of

atomic magnets in a magnetic field has, consequently, been definitely proved by a direct and unmistakable experiment. The value of the moment m_x was calculated from the field strength, the velocity of the atoms, and the length of the path and the width of separation of the lines observed. The value found agreed within the experimental error with the value of the Bohr magneton. The assumption of the nearly instantaneous orientation of the magnet in the field which follows from this is, however, as yet unexplained. The measurements have been extended to other elements since then by Stern.[29] They constitute unquestioned proof of the atomic nature of the magnetic moments, of the reality of the Bohr magneton, and of the quantization of the magnetic moments in a field.

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Books Recommended

a. DEBYE, P.: Marx's "Handbuch der Radiologie," vol. 6, p. 597 ff., 1925. This is the most complete and recent summary of the subject. The material for this chapter largely came from this book. The original article, however, contains far more material than this chapter has space for, and the reader is referred to that source for more complete information.

CHAPTER XI

APPLICATION OF THE KINETIC THEORY TO THE CONDUCTION OF ELECTRICITY IN GASES

104. Introduction.[1]—Probably one of the most spectacular applications of the kinetic theory has been in the field dealing with the conduction of electricity in gases. In fact, rather than this field being merely an application of the theory, it has done a great deal to assist in establishing it. With the discovery of X-rays, the problem attacked by Coulomb and many others unsuccessfully—of how the air conducted electricity—became open to quantitative investigation. This resulted from the considerable conductivity given the air and other gases by the X-rays and the later discovered radiations from radioactive substances. The intense interest excited by these rays led to rapid experimental advances, so that in a few years the following facts were established. The conductivity produced in gases by the agencies above consists in tearing loose from the neutral gas molecules negative electrons, leaving the residual molecule positively charged, or by liberating from a solid or liquid surface near the gas positively or negatively charged bodies. The positively charged bodies of molecular dimensions liberated by heat or radioactive disintegration are probably atoms that have lost an electron. The negative particles usually liberated by the action of heat, light, or a bombardment of the surface with electrical particles are the electrons. In most gases, the electrons when liberated, after some time (the time being a constant of the gas present and depending on the energy of the electron), will attach itself to a neutral molecule. It seems at present likely that both the positive molecule, after losing its electron, and the electron, after attaching to a neutral molecule, attract around themselves further molecules in view of the intense electrical fields present. These charged molecular groups in dry gases were early discovered to be the carriers of electricity in gases under ordinary conditions. They are called in analogy to the carriers of electricity in solutions the gaseous ions. The ions may be described and

studied largely by the velocities with which they move in an electric field. The motion of an ion in a gas under ordinary conditions in an electric field is a uniform velocity of drift. The velocity is proportional to the field strength X over a large range of field strengths (from a few tenths of a volt to 20,000 volts per cm) for a constant pressure. The velocity in cm/sec. in a field of 1 volt/cm is, therefore, a constant and is called the *mobility*. Besides the so-called normal ions, electricity is carried by two other sorts of carriers, electrons and large ions. The electron has a velocity which is not directly proportional to the field and which is thousands of times greater than that of the usual ions.[2,3] It can only be measured under particular conditions. The large ions are charged material particles—dust particles carrying charges. They are characterized by low velocities about one one-hundredth that of the normal gaseous ions. In spite of the claims of certain workers to have observed other classes of ions, the experiments do not warrant the acceptance of such conclusions.[4,5,6,22] In fact, it seems safe to assert that the ions in dry gases under ordinary conditions consist of a single class of carriers of a unique velocity.[7] These velocities vary from gas to gas and differ slightly for positive and negative ions in the same gas. The values have been determined by many different means and these agree fairly well in placing them in a range between about 7 cm/sec. per volt/cm (in H_2 gas where the velocity is greatest) to about 0.2 cm/sec. per volt/cm (in vapors like ethyl ether where the velocities are lowest). The mobility of the ion for a given gas is inversely proportional to the density of the gas from nearly 100 atmospheres down to a few millimeters of gas pressure. This did not seem to hold for negative ions in certain gases below 100 mm, but Wellisch[8] and Loeb[9] have shown that this is due to the complicating presence of free electrons and that the mobility of ions is even here inversely proportional to the pressure. The mobility reduced to constant gas density is known as the *mobility constant*. This constant appears to be almost independent of temperature except at the lowest temperatures studied, a decrease in the constant of 10 per cent being observed at liquid-air temperatures.* In general, the positive ion is slower than the negative ion, although in gases like HCl the reverse is true.[11] Newly gen-

* The experimental results are somewhat contradictory on this point. But the more recent careful experiments of Erikson[10] seem to indicate the correctness of the present statement.

erated positive ions, however, have a mobility equal to the negative ion in gases where the final positive ion is slower. The ions in most cases studied carry a single electrical charge and the Faraday constant for gas ions is closely that observed for univalent ions in electrolysis.[12] Ions of ThD recoil atoms possibly carry a double positive charge for some time after formation.[13] Usually, ions generated with a multiple charge lose all but one charge in the millions of molecular impacts they make in going a cm in the gas.[14]*

The mobility of the ion may be derived from the kinetic theory. In fact, an elementary deduction of this was given in Sec. 22 of Chap. III. The more rigorous derivations of this quantity on the kinetic theory, including certain complications introduced by the forces exerted by the charges on the ions, will form one of the portions of this chapter.

Closely allied to mobility and related to it by a simple relation, is the coefficient of diffusion of the ions, that is, ions of one sign in a gas exert a partial pressure. If the forces due to the charges be ignored (as they may be when ions are present in low concentrations), they will then diffuse through the gas as a result of the partial pressure. As in molecular diffusion, the number diffusing per second N_1 across unit area normal to the concentration gradient $\frac{dn}{dz}$ is given by $N_1 = D\frac{dn}{dz}$, where D is the constant of diffusion governed by the kinetic theory. In ions, the equation for gas molecules is complicated by the attractive forces on the ions. The relation between diffusion and mobility and the value of the coefficient of diffusion D merits being deduced from the kinetic theory.

Again, if ions are generated in a gas the positive and negative ions are present initially in equal numbers. If the charge in the gas is measured at once after the ionizing agent is cut off, a certain number present is obtained. If the number at varying time intervals after the ionization has ceased is measured the number found decreases as the time increases. Experiment shows that, roughly at least, the equation representing this is

* Recently, Erikson has experimental evidence that the ion of one atom will shift its charge to the other, that is, a positive oxygen ion will form a positive acetylene ion in acetylene, the oxygen taking an electron from acetylene and losing its charge, making a neutral oxygen atom and a positive acetylene ion.

$$-\frac{dn}{dt} = \alpha n^2.$$

Here $-\frac{dn}{dt}$ is the rate of disappearance of ions, n is the number per unit volume present at any instant, and α is a constant characteristic of each gas, called the coefficient of recombination. The name of the constant indicates the nature of the cause of disappearance of the ions. Due to their mutually opposite charges or to diffusion, the positive and negative ions come within a close distance of each other. Thus in time they reunite in pairs and the ionization disappears. This process is called the recombination of the ions. The evaluation of the constant α in terms of the kinetic theory will be one of the tasks of this chapter.

The velocity of an electron in unit electrical field, as was said before, is not a constant, that is, the electron has, properly speaking, no mobility. It is convenient, however, to evaluate the velocity of the electron in the field as if it had a mobility and to study the deviations from this in terms of a kinetic-theory interpretation. The theory was first suggested by Townsend[15] and was later amplified by Loeb.[2] The final successful solution of the problem from a theoretical point of view was due to Compton.[3] It will be given in a separate section.

As was stated in the discussion of ionization, the electron liberated by the ionizing process eventually attaches to gas molecules in some gases to make ions.[16,17,18] A study of ion formation indicates that this so-called electron affinity of gas molecules can be characterized by a quantity n, the average number of impacts to cause attachments. The nature of n described above indicates that it was derived by a kinetic-theory analysis. This will constitute another section of the chapter.

Finally, another phenomenon merits a brief treatment. If electrons be liberated from a plate in a rarefied gas, the current which they carry from this plate to one parallel to it but a finite distance away is a function of the voltage. As the voltage increases from zero, the current increases at first in a nearly linear fashion. It gradually, however, departs from linearity, the increase as the voltage increases becoming less. Eventually, it reaches a constant value or saturation for a potential of from 10 to a few hundred volts depending on the pressure. On still

further increasing the voltage, the current remains essentially constant. This constancy is ascribed to the fact that all electrons which leave the plate eventually reach the other plate. At still higher fields the current again begins to increase and eventually increases exponentially, rapidly going to infinity. The explanation given is that in this region the electrons move so fast that they are able to remove the electrons from the gas molecules which they strike. Thus each electron may make α new pairs of ions per cm path and the current increases with distance in the gas according to a law $i = i_o e^{\alpha x}$, where α is the number of new ions formed per cm of path, x the path, and i_o the initial current. Now α is a function of the pressure and field strength. It depends on the ability of the electron to pick up energy from the field and the probability of its ionizing once it has this energy. An expression for α was deduced by Townsend.[19] In view of the recently acquired knowledge of electron kinetics in a gas, this theory must be revised, and the kinetic-theory analysis of it furnishes an excellent means of attack.

Thus the application of the kinetic theory to the field of gaseous ions presents many new and interesting investigations, and it is the purpose of this chapter to set forth the salient features of some of them as briefly and clearly as possible.

105. The Kinetic-theory Analysis of Gaseous-ion Mobilities, Assuming Ions that Are Charged Clusters of Molecules Exerting No Forces on the Gas Molecules Due to Their Charge.—The elementary treatment of gas ion mobilities was given in Sec. 22. The treatment to be given here is on the strict classical kinetic theory. It was due initially to Langevin,[20] but the treatment here given is a modification of it given by H. F. Mayer[21] in a critique of the Langevin theory.

The assumptions underlying this derivation are that the ion is a group of molecules of total mass m which moves in an electrical field due to its charge e. In moving through the field, it is hampered by collisions with gas molecules of mass M, to which by elastic impacts it is continually losing the momentum it has gained in the direction of the field. It exerts no attractive forces on the molecules and both ions and molecules are, for simplicity, assumed spherical. The velocity gained from the field between impacts is further supposed small compared to the thermal velocities of agitation.

Such assumptions lead one to the study of the interchanges of momentum in impact. Assume a molecule M at rest and let an ion of mass m move relatively to M with a velocity u. Assume that the point of impact be A (Fig. 66). The velocity may be resolved into two directions perpendicular and parallel to the surface of M at the point of impact. The tangential component is $u \sin \phi$, where ϕ is the angle between the normal to the surface at A and the direction of motion. The normal component is $u \cos \phi$. The latter component is altered by the impact, while

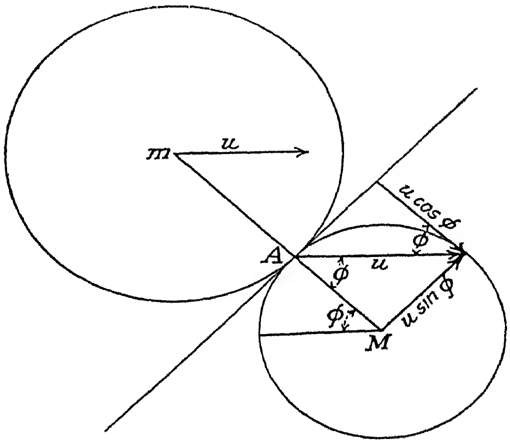

FIG. 66.

the former is not. To this impact the laws of conservation of momentum and energy may be applied. These are

$$mu \cos \phi = mu_1 + MV$$
$$\frac{1}{2}m(u \cos \phi)^2 = \frac{1}{2}mu_1^2 + \frac{1}{2}MV^2,$$

where u_1 is the velocity of m after impact and V is the velocity of M after impact, the initial velocity of M having been 0. Solving for u_1, one obtains $u_1 = \frac{m - M}{m + M}u \cos \phi$. After impact, therefore, the velocity of m is composed of the two components at right angles, $u \sin \phi$ and $\frac{m - M}{m + M}u \cos \phi$. These give a resultant velocity u' of m along the initial direction of motion, that is, the body m persists in its motion in the direction of its motion before impact with a velocity u'. This velocity is given by adding

$$(u \sin \phi) \sin \phi + \left(\frac{m - M}{m + M} u \cos \phi\right) \cos \phi,$$

with the result that

$$u' = u\left(\sin^2 \phi + \frac{m - M}{m + M} \cos^2 \phi\right).$$

The average persistence is found by taking the average of u' for all values of ϕ. This is done by multiplying by the chance of an angle ϕ, between ϕ and $\phi + d\phi$, which is $2 \sin \phi \cos \phi d\phi$, and integrating ϕ from 0 to $\frac{\pi}{2}$. Hence,

$$\bar{u}' = 2u \int_0^{\frac{\pi}{2}} \left(\sin^2 \phi + \frac{m - M}{m + M} \cos^2 \phi\right) \sin \phi \cos \phi d\phi.$$

$$\bar{u}' = \frac{m}{m + M} u = \mu u,$$

where

$$\mu = \frac{m}{m + M}.$$

If the molecule M was not at rest but had components of motion U, V, and W, while the ion m had components u, v, w, the u and u' used before would be replaced by the relative velocities $u - U$ and $u' - U$. These lead at once to a value of $\bar{u}' = \dfrac{mu + MU}{m + M}$. Similar relations hold for v' and w', the velocities along the v- and w-axes after impact. The average loss of velocity in impact is, therefore,

$$u - \bar{u}' = \frac{M}{m + M} (u - U).$$

For simplicity, assume that all of the N gas molecules in unit volume have the velocity components U, V, W, while the gas ion moves through the gas with the uniform velocity components u, v, w. The number of impacts per second suffered by the ion is then given by the mean collision frequency, which is given by $\pi s^2 Nc$. Here $s = r + R$, the sum of the radii of ion and molecules, and c is the relative velocity of the ion and the molecules. This is given by

$$c = \sqrt{(u - U)^2 + (v - V)^2 + (w - W)^2}.$$

The loss of velocity of the ion m per second with the number of collisions per second given above is

$$(u - \bar{u}')Ns^2\pi c.$$

Now the velocity components of the molecules are not all equal and the components of the ion change at each impact. If df be the chance that the ionic velocities lie between u and $u + du$, v and $v + dv$, and w and $w + dw$, and if dF be the chance that the molecular velocities U, V, and W lie between U and $U + dU$, V and $V + dV$, and W and $W + dW$, then the mean loss of the velocity of the ion per second in its path through the gas is given by

$$\int\int (u - \bar{u}')\ \pi s^2 N c df dF.$$

The ion, on the other hand, is gaining a velocity each second along the u-axis from the force exerted by the field on its charge. Call this increase in velocity per second $b = \frac{K}{m}$, that is, b is the acceleration of the ion, K is the force, and m the mass of the ion. At equilibrium the ion is moving with a uniform velocity of drift, and hence the *average discontinuous decelerations* due to impacts must equal the continuous acceleration due to the field. Thus

$$mb = K = m\int\int (u - \bar{u}')N\pi s^2 c df dF,$$

or

$$K = \frac{mM}{m + M}\int\int (u - U)N\pi s^2 c df dF.$$

If the gas, as a whole, is at rest, that is, if mass motion is absent, df and dF can be replaced by their equivalents in the Maxwell distribution law. This law expressed, using the Boltzmann constant h (see Sec. 43), gives for df and dF the values,

$$df = \left(\frac{hm}{\pi}\right)^{3/2} e^{-hm[(u-\omega)^2+v^2+w^2]} du dv dw$$

where ω is the average velocity of drift of the ion in the u direction.

$$dF = \left(\frac{hM}{\pi}\right)^{3/2} e^{-hM(U^2+V^2+W^2)} dU dV dW.$$

Since ω is very small compared to u (some tens of cm per second compared to 4×10^4 cm per second or more), the higher powers of $\frac{\omega}{u}$ can be neglected, and so

$$df = \left(\frac{hm}{\pi}\right)^{3/2} e^{-hm(u^2+v^2+v^2)} (1+2hmu\omega) du dv dw,$$

Putting these quantities into the expression for K, on integration,

$$K = \frac{4\omega}{3} N\pi s^2 \sqrt{\frac{4}{h\pi}\frac{mM}{m + M}}.$$

The integrations above are more easily accomplished if the new variables below are used.

$$u = X + \frac{M}{m + M} x \qquad U = X - \frac{m}{m + M} x$$

$$v = Y + \frac{M}{m + M} y \qquad V = Y - \frac{m}{m + M} y$$

$$w = Z + \frac{M}{m + M} z \qquad W = Z - \frac{m}{m + M} z$$

$dudvdwdUdVdW = dxdydzdXdYdZ.$

From the equation after integration one has at once that the velocity of the ion ω is

$$\omega = \frac{3}{4}\frac{K}{\pi s^2 N}\sqrt{\frac{h\pi}{4}\frac{m + M}{mM}}.$$

This is a general equation and makes it possible to obtain either the mobility or the diffusion coefficient. If the K above designates the force on an ion Xe, where X is the field strength and e is the charge, ω is the velocity of the ion in the field. If K is the force on the ion due to the partial pressure of the ions, ω is the velocity of diffusion of the ions.

To reduce the expression for the mobility of the ion to a handier form, K may be replaced by eX, and it should be remembered that the square of the average speed $\bar{c}^2$ is equal to $\frac{4}{\pi hM}$ for the molecules. Thus

$$\omega = \frac{3}{4}\frac{eX}{\pi s^2 N}\frac{1}{\bar{c}M}\sqrt{\frac{m + M}{m}}.$$

If one had used $(\bar{c}')^2 = \frac{4}{\pi hm}$ for the *ions*, one would have

$$\omega = \frac{3}{4}\frac{eX}{\pi s^2 N}\frac{1}{\bar{c}'m}\sqrt{\frac{m + M}{M}}.$$

$\bar{c}$ and $\bar{c}'$ may be replaced by C and C' for the molecules and ions, that is, by the square roots of the mean square speeds, by remembering that $\bar{c} = \frac{C}{\sqrt{\frac{3\pi}{8}}} = \frac{C}{1.085}$ (see Sec. 35). Again, $\frac{1}{\pi N s^2}$ may

be called the mean free path of the ion in the gas. This is not strictly true, as may be seen from Secs. 17 and 37. $\frac{1}{\pi s^2 N}$, however, may be replaced by the symbol λ and, for short, designated as the mean free path. The equations above become, on making these changes,

$$\omega = 0.815 \frac{Xe\lambda}{MC} \sqrt{\frac{m + M}{m}}$$

and

$$\omega = 0.815 \frac{Xe\lambda}{mC'} \sqrt{\frac{m + M}{M}}.$$

Since $\frac{\omega}{X} = k$, the mobility of the ion,

$$k = 0.815 \frac{e}{M} \frac{\lambda}{C} \sqrt{\frac{m + M}{m}}$$

$$k = 0.815 \frac{e}{m} \frac{\lambda}{C'} \sqrt{\frac{m + M}{M}}.$$

Mayer, in the article where this derivation is given, deduces the expression of Lenard from the reasoning applied here. The only essential difference, according to Mayer, is the fact that Lenard takes into account the possibility of the velocity in the direction of the field between impacts, due to the field becoming appreciable relative to the velocity of agitation. In general, this correction is not necessary. Its introduction complicates the derivation and makes discussion of a more involved equation tedious. As neither of these theories is entirely correct, the small difference is of no importance. In any case, the only essential change is one in the mass factor. Both forms of the equation deduced above are useful. They give the mobility of the ion terms of the charge and free path of the ion divided by the mass and root mean square of the velocity of the gas molecules in one case, and divided by the mass and root mean square velocity of the ion in the other case. The first equation is best in discussing the value of the mobility of the ion, as C and M are known, and the factor for the mass of the ion changes k but little. The second equation makes it possible to carry the equation over to a carrier like the electron for further discussion, for all that is needed is to introduce the values for λ, C', and m for an electron into the equation.

To deduce the expression for the coefficient of diffusion of ions, the force K must be determined in terms of the diffusion coeffi-

cient. The expression for the number of ions n diffusing across 1 cm^2 of area per second is given by

$$n = D\frac{dn'}{du},$$

where n' is the number of ions per cm^3, $\frac{dn'}{du}$ is the gradient in the u direction, *i.e.*, the direction of diffusion, and D is the coefficient of diffusion. Call ω the velocity of diffusion along u. Then $n = \omega n'$, or $\omega = \frac{D}{n'}\frac{dn'}{du}$. If the ions exert a partial pressure, as gas molecules do, one may write that $p = an'$, where a is a constant, and $dp = adn'$. Thus $\frac{dp}{p} = \frac{dn'}{n'}$. The only doubt about this approximation is that the charges of the ions exert a force of repulsion on each other. For gaseous ionization experiments, charge densities of more than 10^6 ions per cm^3 are rare. This separates the ions, on the average, by distances of the order 5×10^{-3} cm from each other. The forces of repulsion at this distance, even on an inverse-square law, are small and may be neglected in some cases. Replacing $\frac{dn'}{n'}$ by its equivalent, one has the velocity of diffusion given by

$$\omega = \frac{D}{p}\frac{dp}{du}.$$

Now the force acting on the ions is the pressure times the area. Since the number of ions n diffusing was taken per unit area the force on a cm^3 of ions due to the pressure gradient $\frac{dp}{du}$ is

$$\frac{dp}{du} \times 1 \text{ cm} \times 1 \text{ cm}^2,$$

that is, the force on 1 cm^3 of ions is $\frac{dp}{du}$. The force on one ion will be

$$\frac{1}{n'}\frac{dp}{du} = K = \frac{p\omega}{n'D}.$$

Placing this into the expression for ω,

$$\omega = \frac{3}{4}\frac{\frac{p\omega}{n'D}}{\pi s^2 N}\sqrt{\frac{h\pi}{4}\frac{m+M}{mM}},$$

calling $\frac{1}{\pi s^2 N} = \lambda$, and inserting M and C for molecules for h,

$$D = 0.815 \frac{p\lambda}{MC}\sqrt{\frac{m+M}{m}}.$$

Since $\frac{p}{n'} = \frac{1}{3}m(C'^2) = \frac{1}{3}MC^2$ if ions exert a gas pressure,

$$D = 0.815 \frac{\lambda C}{3}\sqrt{\frac{m+M}{m}}.$$

For $m = M$,

$$D = 0.815 \frac{1.41}{3} \lambda C = 0.384\lambda C.$$

The equation for the diffusion of molecules where the masses were the same as the masses of the molecules diffused into was found on simple kinetic theory to be $D = \frac{1}{3}\bar{c}L$. Since $L = \frac{1}{\sqrt{2}\pi\sigma^2 N}$, $\lambda = L\sqrt{2}$ and the above equation becomes $D = 0.217\lambda C$, which is roughly the same as the one for ions. If the expression for the mobility of the ion from this equation be divided by the expression for D,

$$\frac{k}{D} = \frac{0.815 \frac{e}{M}\frac{\lambda}{C}\sqrt{\frac{m+M}{m}}}{0.815 \frac{C}{3}\lambda\sqrt{\frac{m+M}{m}}},\ \text{then}$$

$\frac{k}{D} = \frac{3e}{MC^2}$. Multiplying top and bottom of the right-hand side of the equation by N, the number of molecules per cm,[3] then

$$\frac{k}{D} = \frac{Ne}{\frac{1}{3}NMC^2} = \frac{Ne}{P},$$

that is, the mobility k divided by the diffusion coefficient D is the Faraday constant divided by 22,400 and the pressure P corresponding to N. If the value of e for gaseous ions is the same as for electrolytic ions the quantity $\frac{Pk}{D}$ should give the Faraday constant for monavalent ions divided by 22,400. This is, in fact, the case. Experiment gives $k = 1.8$ cm/sec per volt/cm for negative ions in air, that is, 540 cm/sec. per E.S.U/cm, while

it gives D for negative ions in air as $D = 0.043/\text{cm}^2 \times \text{sec.}$, when $p = 1 \times 10^6$ dynes/cm².

Thus
$$p\frac{k}{D} = \frac{540 \times 10^6}{0.043} = 1.25 \times 10^{10} \text{ E.S.U.}$$

Now N is 2.71×10^{19}, and e is 4.77×10^{-19} E.S.U.; whence Ne is 1.29×10^{10} E.S.U. This agreement is well within the accuracy of the measurements of D. It is therefore possible to assume that ions exert a partial pressure like a gas, to assert that they carry the same charge as univalent ions, and to calculate D from k, which can be readily measured by $D = 0.0236k$, when k is in cm/sec. per volt/cm.

106. Test of the Simple Ion Theory and Further Formulation of the Mobility Problem.—One more point in connection with diffusion of ions leads to a test of this theory. If the diffusion coefficient of ions in CO_2 is compared with the coefficient of molecules of N_2O into CO_2, a nearly equivalent case, it is found that D for these ions is 0.023, while for CO_2 molecules it is 0.15 to 0.1. Thus the ions diffuse about one-sixth as fast as the uncharged molecules diffuse.

This must mean that λ for the ions is not the same as for uncharged gas molecules. A discrepancy in a similar direction is brought out if k is computed for ions in air from the equation

$$k = 0.815\frac{e}{M}\frac{\lambda}{C}\sqrt{\frac{m+M}{m}}.$$

For this purpose assume $M = m$, that is, that the ion has molecular dimensions. The λ here used is $\sqrt{2}$ times the L from kinetic theory for air molecules and, as the $\sqrt{\frac{m+M}{m}}$ is $\sqrt{2}$ for the case where $M = m$, $k = 1.63\frac{e}{M}\frac{L}{C}$. Putting in the accepted kinetic-theory values for L, M, C, and e a computed mobility for ions of 11.7 cm/sec. per volt/cm is obtained for air ions. The observed value for air is 1.8 cm/sec. per volt/cm for negative ions and 1.4 cm/sec. per volt/cm. for positive ions. It is probable that these observed values will have to be increased by a factor of 1.21, owing to a consistent error in mobility measurements.[23,7] In any case the mobility is nearly one-fifth that computed.

This can mean that the value of λ assumed, together with the other constants, is not that for charged molecules which do not

exert any forces on neutral molecules in virtue of their charge as they move through the gas. The action of the charge of the ion on neutral molecules may be explained in two ways. The charge on the ion may attract neutral molecules in virtue of its field (that is, it may induce a charge on an uncharged molecule) or it may act on electrical dipoles already present in the molecules (see Chap. X, Sec. 96). In doing so it will undergo exchanges of energy and momentum with these molecules, without impact. It may also suffer a decreased mean free path, as, owing to the attractive forces, an impact that was not predestined to occur had there been no forces will take place. This type of action can be explained as causing an apparent increase in s, the sum of the radii of ion and molecule due to the attractive forces. Thus, as s increases, λ, the free path, will decrease. Such a theory is known as the *small-ion theory* and was independently developed by Wellisch[24] and Sutherland[25] in 1909. The earliest explanation of the small mobility offered was the alternative to the view above, namely, that the charge on the ion was so intense that the neutral molecules were bound to the molecule with the charge and that this binding went on until the force field around the ion was practically ineffective beyond the ion. Such an ion is called the *cluster ion*. The number of molecules in the cluster has been estimated at from 6 to 30 molecules by various workers on different theories. The cluster formation would then change the factor $\sqrt{\frac{M+m}{m}}$ used above, and the increase in s^2 due to the cluster would make a corresponding decrease in λ.

The two points of view have been the cause of controversy for many years. In fact, experimental evidence of a definite nature was lacking until the recent experiments of Erikson and of Loeb.[26,11] These definitely indicate the formations of clusters of a more or less labile type in certain gases. The cluster type of action is not alone able to account for all the phenomena observed. It is probable from the nature of the forces acting that the small ion type of activity also occurs and the correct theory of mobilities must include both types of action. The question really hinges on the law of force between ions and neutral molecules. Were the forces weak but active over a long range, the result would be the small ion. Were they large and did they fall off rapidly with the distance, the result would be a cluster ion. The beautiful work of Debye (Chap. X)[27] on the dielectric

constants and on the forces on ions in solutions has in recent years led to some justification of the view that the action of the field of the ion on a neutral molecule could, to a large extent, be considered as the attraction of a point charge on the induced or oriented dipole of a dielectric body in its neighborhood, that is, it is possible to compute the forces between an ion and a molecule, assuming that the molecule is a dielectric at a distance r from the ion, whose dielectric constant in bulk is a measure of its polarization. Since the attraction of a point charge on a dipole varies as $\frac{1}{r^3}$ and the field producing the dielectric displacement varies as $\frac{1}{r^2}$, the force between ion and the molecular dipole produced by the field would vary as $\frac{1}{r^5}$. This would hold whether the polarization of the molecule were due to a dielectric displacement or the orientation of a permanently dipolar molecule in the field of the ion. Both effects would be proportional to the ionic field at a distance r $\left(i.e., \text{both would vary as } \frac{1}{r^5}\right)$.

In fact, later evidence from the values of the mobility computed, making use of this law, will show that, except for errors of the order of magnitude of the differences in mobilities between the positive and negative ions, this law of attraction suffices. It does not suffice when the molecules and ions are within a molecular radius or two of each other, as the difference between positive and negative mobilities which cannot be explained in this manner shows. The reason for this is adequately discussed in a paper by Loeb.[26]

As constant use will be made of this law of force, it will be deduced at this point. The field F at any point between two plates with a density of electrification of opposite signs σ is given by $F = 4\pi\sigma$. If a dielectric whose constant is D is placed between them, the field F' is now $\frac{F}{D} = F'$. This apparent loss of intensity is due to the absorption of the lines of force by charges in the dielectric, that is, it is due to a charge induced in the medium by the field and is proportional to it. Symbolically, this is designated by the relation

$$F - F' = 4\pi\sigma',$$

where σ' is the surface density equivalent to the charge produced on the material. From this it follows that

$$\frac{F - F'}{F'} = D - 1 = \frac{4\pi\sigma'}{F'},$$

or

$$\sigma' = \frac{F'(D - 1)}{4\pi}.$$

For a gas between the two plates σ', the charge density multiplied by the area of the plates and mutliplied by the distance between them, or σ' times the volume between the plates, gives the equivalent electrical moment of all the charges in the gas. This divided by the volume of the gas between the plates then gives M, the electrical moments of the gas molecules between the plates per unit volume, that is, $\sigma' = M$, the moment of the polarized gas per unit volume. Hence one has $M = \frac{(D - 1)F'}{4\pi}$. Now the electrical moment of one molecule is $\mu = \frac{M}{N}$, where N is the Loschmidt's number. Thus the moment of a molecule can be set as

$$\mu = \frac{(D - 1)F'}{4\pi N}.$$

Since in this case F', the acting field, is produced by a charged molecule (an ion), the field can be regarded (except at very small distances) as due to a charge located at a single point. F' is then given by $\frac{e}{r^2}$ where e is the charge and r the distance from the ion. Thus $\mu = \frac{(D - 1)}{4\pi N}\frac{e}{r^2}$. It is well known that for a dipole of moment μ the force with which it is acted on by a point charge r cm distant is given by $f = \frac{2\mu e}{r^3}$. Thus the force between ion and molecule is given by the expression

$$f = \frac{(D - 1)e^2}{2\pi N r^5}.$$

The potential energy of the ion at a distance r from the molecule due to the field is given by

$$W = \int_r^\infty \frac{(D - 1)}{2\pi N}\frac{e^2}{r^5}dr = -\frac{(D - 1)}{8\pi N}\frac{e^2}{r^4}.$$

The potential is negative, which means that the work which the molecule can do in being moved to infinity is negative.

From this law of force it is possible to estimate the size of the ion cluster, for, in order to be stable, the cluster must have a sufficient radius so that r, the distance between the center of the ion and center of the molecule (assuming the law to hold at such distances), is small enough so that the potential energy of the ion and molecule is equal to the average energy of thermal agitation. If the kinetic energy of agitation is greater than the potential energy, on the average, the molecule will not describe a closed orbit about the ion, and thus it will not be captured and bound. Hence, for a cluster ion, the radius r_c must be such that $\frac{W}{KE}$, the potential over the kinetic energy, is greater than unity. Now $W = \frac{(D - 1)e^2}{8\pi N r_c^4}$, and $KE = \frac{1}{2}MC^2$, thus

$$\frac{W}{KE} = \frac{(D - 1)e^2}{4\pi NMC^2 r_c^4} = \frac{(D - 1)e^2}{12\pi p r_c^4},$$

since $p = \frac{1}{3}NMC^2$. D for air is 1.0006, $p = 1 \times 10^6$ dynes/cm², and $e = 4.8 \times 10^{-10}$. If r_c be taken as $r_c = 3.3 \times 10^{-8}$, which is the value of the molecular diameter in air and corresponds to an ion composed of a layer of molecules one molecule deep about the central charged molecule, one obtains $\frac{W}{KE} = 3.1$. Thus a monomolecular layer cluster could be stable. Were the nucleus and molecules spheres of the same size, the maximum number of molecules in a stable cluster would be 12. A cluster of more than 12 molecules would require another layer, for 12 molecules is all that can be placed around a sphere of the same size. A larger cluster would perhaps be a little less than double r, for the next layer of molecules, and r^4 would be 16 times as great. This would give $\frac{W}{KE} = 0.19$, and the outer layer would not be stable. It is very unlikely that the ion cluster numbers more than 12 molecules and evidence seems to point to possibly as few as one or two more or less permanent companions to the charged molecule. In a recent paper Hassé[40] explains the difference between the mobilities of positive and negative ions on such a view. The negative ion has a layer of molecules about an electron, the positive ion a single layer of molecules about a charged molecule.

107. Deduction of an Expression for the Shortening of the Mean Free Path Due to Attractive Forces—a Typical Small-ion Theory.—With the adoption of the law of force as probably obtaining in order of magnitude, it becomes possible to compute the force of attraction and consequently the apparent decrease of the mean free path of the ions due to such a law. In general, a method devised by Wellisch[24] will be used. Certain errors were inherent in the original deduction and they will, accordingly, be corrected for in this text. Certain objections to Wellisch's theory as a small-ion theory may also be urged. However, the equation as deduced is able to give the mobilities of the correct order of magnitude without any arbitrary assumptions as to size of cluster, and is thus an improvement on previous theories. It is also being included as it makes it possible to see how ionic or intermolecular forces can influence the mean free path.* The more complete and correct mobility equation derivations are entirely too involved to reveal the method of attack clearly, and thus will not be derived, although their conclusions will be discussed.

Wellisch starts out with the mobility equation in its elementary form $k = \frac{e}{m}\frac{\lambda}{\bar{c}_1}$, and proceeds, after assigning λ the value for the mean free path of an ion of mass m in a gas of molecules of mass M, to find how the forces of attraction influence the mean free path. In the present deduction the equation of Langevin,

$$k = 0.815\frac{e}{M}\frac{\lambda}{C}\sqrt{\frac{m+M}{m}},$$

will be used as a basis, and the effect on λ of the forces of attraction between ion and molecule will be calculated as Wellisch calculated them. The law of force between ion and molecule is $F = \frac{(D-1)e^2}{2\pi N r^5}$, as deduced above, where r is the distance between the ion and the molecule. This gives the potential energy at r, $W_r = \frac{(D-1)e^2}{8\pi N r^4}$. Consider, for simplicity, that the molecule is at rest and that the ion approaches it with the total relative velocity. Call U the velocity of the ion at infinity and u the velocity at the point of closest approach. The ion will come

* This deduction parallels that of Sutherland Sec. (62) and without the complicated mathematics arrives at a similar result.

from infinity, increasing its velocity as it approaches, describe an orbit about the fixed molecule and depart, as it is not captured. Where the ion and the molecule separate after the distance of closest approach, the orbit is an hyperbola, the initial velocity U being directed along the asymptote (see Fig. 67). The law of conservation of energy says that in such an encounter

$$\frac{1}{2}m(u^2 - U^2) = W',$$

where W' is the relative potential energy of the ion and the molecule. W' is related to the potential W, the actual potential energy

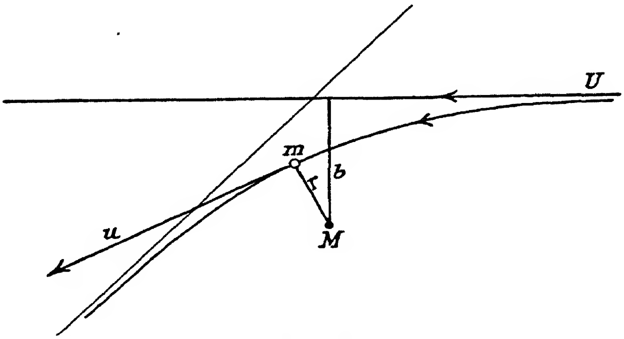

FIG. 67.

of the ion given above, by a simple relation. Call M the mass of the molecule and C its velocity, while C_1 is the velocity of the ion of mass m. Then

$$W_r = \frac{mC_1^2}{2},$$

while

$$W' = \frac{mC_1^2}{2} + \frac{MC^2}{2}.$$

However,

$$mC_1 = MC,$$

or

$$C = \frac{m}{M}C_1.$$

Thus,

$$W' = \frac{mC_1^2}{2}\left(1 + \frac{m}{M}\right)$$
$$= \frac{m + M}{M}W_r.$$

Accordingly,

$$\frac{1}{2}m(u^2 - U^2) = \frac{m + M}{M}W.$$

The law of conservation of moment of momentum furthermore requires that $ru = bU$, for b is the radius of rotation about M when the velocity is U, and r is that when the velocity is u. Thus

$$r^2 = b^2\left(\frac{U}{u}\right)^2,$$

and, as

$$u^2 = 2\frac{m + M}{mM}W_r + U^2,$$

$$r^2 = b^2\left(\frac{U^2}{2\frac{M + m}{mM}W_r + U^2}\right)$$

$$= b^2\left(1 + \frac{2W_r}{\frac{mM}{m + M}U^2}\right)^{-1}.$$

Now the condition for a collision is that s, the sum of radii of ion and molecule, should be equal to or greater than r. Thus for a collision, s^2 must be such that

$$s^2 \geq b^2\left(1 + \frac{2W_s}{\frac{mM}{m + M}U^2}\right)^{-1},$$

that is, for impact, the square of perpendicular from the molecule on the initial direction of motion of the ion must be equal to or less than the original sum of radii of ion and molecule multiplied by the factor

$$\left(1 + \frac{2w_s}{\frac{mM}{M + m}U^2}\right) \quad \text{or} \quad b^2 \leq s^2\left(1 + \frac{2W_s}{\frac{mM}{M + m}U^2}\right)$$

Thus, with no forces acting, collision occurred when $b \leq s$. With forces, b^2 can be equal to or less than s^2 multiplied by a factor greater than unity by the ratio $\frac{W_s}{\frac{1}{2}\frac{mM}{M + m}U^2}$, to be defined later.

Thus the s_f, when forces of the form above act, is related to the s when no forces act by the equation

$$s_f^2 = s^2 + \frac{2s^2W_s}{\frac{mM}{M + m}U^2}.$$

Now

$$\frac{1}{2}mU^2 = \frac{1}{2}mC_1^2\left(1 + \frac{m}{M}\right)$$

$$U^2 = C_1^2\left(1 + \frac{m}{M}\right)$$

$$\left(\frac{MU^2}{m + M}\right)\frac{m}{2} = \frac{mC_1^2}{2} = \frac{MC^2}{2},$$

where $\frac{MC^2}{2}$ is the kinetic energy of agitation of the gas molecules.

Thus $s_f^2 = s^2\left(1 + \frac{2W_s}{MC^2}\right)$. The s^2 in Langevin's λ is, accordingly, to be replaced when forces act by s_f^2, so that Langevin's equation becomes, for this case,

$$k = 0.815\frac{e}{M}\frac{\lambda}{\left(1 + \frac{2W_s}{MC^2}\right)C}\sqrt{\frac{m + M}{m}},$$

the value of k thus being merely divided by the quantity $\left(1 + \frac{2W_s}{MC^2}\right)$. This is unity plus the ratio of the potential energy of ion and molecule at impact to the kinetic energy of thermal agitation. Substituting for W_s, this becomes

$$k = 0.815\frac{e}{M}\frac{\lambda}{C}\frac{\sqrt{\frac{M + m}{m}}}{\left\{1 + \frac{(D - 1)e^2}{4\pi NMC^2s^4}\right\}}.$$

Now it was found that the ratio of potential to kinetic energies for a molecular ion in contact with a molecule (*i.e.*, for a small ion at impact) was 3.1. Thus, the Wellisch factor reduces k from the value 11.7 calculated for a forceless ion to $\frac{11.7}{4.3} =$ 2.7 cm/sec. per volt/cm. This value is in fairly good agreement in order of magnitude with the observed value. The criticisms of this theory lie in the application of the factor $\frac{2W_s}{MC^2}$ as calculated above to a small-ion theory, for the value of this factor, as shown before, suggests a cluster formation. Another minor weakness of this theory is that it neglects the loss of momentum of the ion gained in the field in cases where its path is curved, and it thus exchanges momentum with the molecule,

but does not actually collide. The amount of error introduced by this neglect is of the order of 10 per cent, as a rigorous calculation by J. J. Thomson shows (see Sec. 108). The change in k by such a correction would be less than 10 per cent and the k above would become 2.4 cm/sec. per volt/cm. The theory is interesting, however, in that it shows that the forces will, with an elastic-impact theory, yield a value of the mobility which is in fair agreement with experiment. It is to be noted in passing that the mobility is a function of the charge e of the ion in both this and the Langevin equation. It is, however, less so than appears on the surface, for if the ion cluster depends on the value of e, or if the attractive forces do, they will bring in e to increase s^2, and thus introduce a factor dependent on e in the denominator.

108. The Mobility Deduced from the Rate of Energy Loss of the Ion to the Molecules of the Gas—Theory of J. J. Thomson.[28]— In 1924, the writer[29] utilized a somewhat more accurate deduction of J. J. Thomson[28] for the change in λ produced by the charge. This placed in the Langevin equation showed some properties of such interest that it merits a short discussion. J. J. Thomson starts with the assumption of an inverse fifth-power law of force and applies the equations of dynamics in a more rigorous fashion than does Wellisch.[24]

If two bodies of masses M_1 and M_2 collide or exchange momentum in an encounter, the kinetic energy transferred from one to the other is given by

$$\frac{4M_1M_2}{(M_1 + M_2)^2}T \sin^2 \theta.$$

Here 2θ is the angle through which their relative velocity is turned, and $2T$ is the momentum of the system multiplied by the relative velocity and the cosine of the angle between the velocities. If either is at rest, $2T = MV^2$ for the moving particle. It is merely necessary for the later development to determine the rate of loss of energy of the ion to the molecules it encounters in virtue of its attractive forces. To do this, it is essential to derive the value of the energy transfer gained from the field to neutral molecules in going through a cm of gas. To evaluate this, θ must first be calculated for an encounter on the inverse fifth-power law assumed. Let

$$F = \frac{(D - 1)e^2}{2\pi N r^5} = \frac{A}{r^5}.$$

Then assuming the ion fixed and the molecule describing an orbit around it, the differential equation of motion for a central force varying inversely as the fifth power of the distance as given by classical dynamics[30] is

$$\frac{d^2u}{d\theta^2} - u = \frac{Au^3}{mh^2}.$$

In this equation 2θ is the angle through which the relative velocity is turned, $u = \frac{1}{r}$, m is the mass of the particle, and $h^2 = V^2p^2$. V is the initial velocity of the molecule relative to the ion, and p is the perpendicular distance from the ion onto the initial velocity of the molecule. In the case in question two bodies of masses M_1 and M_2 are being dealt with and m, the mass of a single particle, must be replaced by the factor $\frac{M_1M_2}{M_1 + M_2}$ from the laws of dynamics. Bearing these facts in mind, the equation above yields, on multiplying by $\frac{2du}{d\theta}$ and integration,

$$mh^2\left[\left(\frac{du}{d\theta}\right)^2 + u^2\right] = \frac{Au^4}{2} + mV^2$$

whence

$$\left(\frac{du}{d\theta}\right)^2 = \frac{Au^4}{2mh^2} - u^2 + \frac{mV^2}{mh^2}.$$

At the apse $\frac{du}{d\theta} = 0$. Thus the apsidal distances are the roots of the equation above when $\frac{du}{d\theta} = 0$, that is, they are the roots of

$$u^4 - 2\frac{mV^2p^2}{A}u^2 + \frac{2mV^2}{A},$$

$$u^2 = \frac{2mV^2p^2}{2A} \pm \frac{\sqrt{\frac{4m^2V^4p^4}{A^2} - \frac{8mV^2}{A}}}{2}.$$

Thus to have real roots,

$$p^4 \geq \frac{2A}{mV^2}.$$

For values of p less than this there will be no apsidal distances and the bodies will collide. It is here that J. J. Thomson makes

an assumption that is perhaps to be questioned. He assumes that on such impacts the collisions are like direct collisions for elastic particles, and that in such impacts the velocities will be reversed and the bodies will retrace their paths. Thus with the relative velocities unaltered in magnitude and reversed in direction, 2θ will be π, and $\sin\theta$ will be unity that is, for a perpendicular distance from the ion onto the initial path of the molecule less than $\frac{2A}{mV^2}$ an apse cannot exist, or rather is imaginary. What the existence of no apsidal distances means is that, instead of the molecule circling about the ion in an orbit for values of p less than this critical value, the molecule will fall into the ion. Thomson assumes that on such an impact the motion will be largely along the line of centers. Were this true, his assumption would be fulfilled and the bodies would reverse their velocities. This condition of central impact would hold if the ion and the molecule were merely points compared to the critical value of p. If, however, the sum of radii of ion and molecules s were an appreciable fraction of p, then the impacts would take place between spherical surfaces before the molecular center had a chance to complete enough of its path to make the direction of motion correspond to line of centers. Under these conditions the impacts would be far from central and the exchange of momentum would differ radically. Now calculation will show, using values of A, m, and V^2 for ions in air, that p is of the order of two to four times s for two molecules. Thus, in general, Thomson's assumption is not correct. This is especially serious in view of the fact that the greater values of p inside of this limit are more frequent than the smaller ones. In a very much more rigorous and complete derivation from a different point of view, Langevin studies the case of collisions between spherical molecules when it is less. The result of this study leads him to an average value for the energy exchange in such impacts.

Accepting Thomson's assumption as correct for the present, one proceeds as follows. If b be the value of u at an apse,

$$\frac{Ab^4}{2mh^2} - b^2 + \frac{mV^2}{mh^2} = 0$$

or

$$\frac{Ab^4}{2mV^2p^2} - b^2 + \frac{1}{p^2} = 0;$$

whence,

$$\begin{aligned}\left(\frac{du}{d\theta}\right)^2 &= \frac{A}{2mp^2V^2}(u^4 - b^4) - (u^2 - b^2)\\ &= \frac{A}{2mV^2p^2}(b^2 - u^2)\left[\frac{2mp^2V^2}{A} - (b^2 + u^2)\right]\\ &= \frac{A}{2mp^2V^2}(b^2 - u^2)\left(\frac{2mV^2}{b^2A} - u^2\right).\end{aligned}$$

This equation is now to be solved for u as a function of θ. To integrate it, put $u = b \sin \Psi$. This gives

$$\left(\frac{d\Psi}{d\theta}\right)^2 = \frac{Ab^2}{2mb^2p^2V^2}\left(\frac{1 - \sin^2\Psi}{\cos^2\Psi}\right)\left(\frac{2mV^2}{Kb^2} - b^2 \sin^2 \Psi\right)$$

and

$$d\theta = \left(\frac{2mV^2p^2}{A}\right)^{1/2} \frac{d\Psi}{\left(\frac{2mV^2}{Ab^2} - b^2 \sin^2 \Psi\right)^{1/2}}.$$

Putting $k^2 = \dfrac{Ab^4}{2mV^2}$, the equation may be reduced to the form

$$d\theta = (k^2 + 1)^{1/2} \frac{d\Psi}{(1 - k^2 \sin^2 \Psi)^{1/2}}.$$

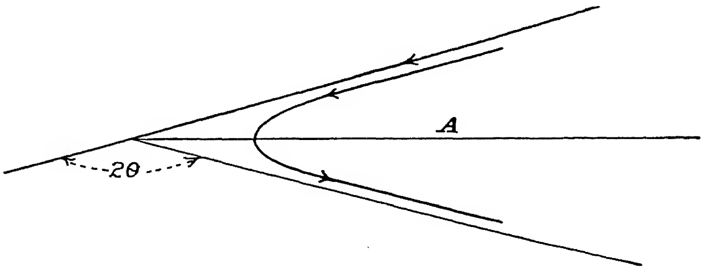

FIG. 68.

From Fig. 68, it is seen that the angle 2θ through which the relative velocity is turned is

$$\pi - 2\int_0^b \frac{d\theta}{du}\,du = \pi - 2\int_0^{\frac{\pi}{2}} \frac{d\theta}{d\Psi}\,d\Psi,$$

for $u = b \sin \Psi$ is equal to b when $\Psi = \dfrac{\pi}{2}$.

Thus 2θ is given by

$$2\theta = \pi - 2\int_0^{\frac{\pi}{2}} (1 + k^2)^{\frac{1}{2}} \frac{d\Psi}{(1 - k^2 \sin^2 \Psi)^{\frac{1}{2}}}$$
$$= \pi - 2(1 + k^2)^{\frac{1}{2}}F(k).$$

$$\text{Thus } \sin\theta = \sin\left[\frac{\pi}{2} - (1 + k^2)^{\frac{1}{2}}F(k)\right]$$
$$= \cos\,(1 + k^2)^{\frac{1}{2}}F(k).$$

The expression for the transfer of kinetic energy given at the beginning of the discussion is then

$$KE = \frac{4M_1M_2}{(M_1 + M_2)^2}\, T \sin^2\theta$$
$$= \frac{4M_1M_2}{(M_1 + M_2)}\, T \cos^2\,(1 + k^2)^{\frac{1}{2}}F(k).$$

Thus the energy transfer at any impact is found as a function of m, p, and V for the system. With this loss per impact, the average energy loss per cm of path of an ion in the gas may at once be calculated. For N molecules per cm³ in the gas an ion will encounter $2\pi Npdp$ ions per cm path at a distance between p and $p + dp$. The energy loss E_1 per cm path in the gas for apsidal impacts is therefore

$$E = \frac{4M_1M_2}{(M_1 + M_2)^2} T \int \cos^2\{(1 + k^2)^{\frac{1}{2}}F(k)\}2\pi Npdp.$$

To this integral must be added the energy loss for all the non-apsidal impacts included in the interval from 0 to $p = b = \sqrt[4]{\frac{2A}{mV^2}}$. The second term, which is the one for E_1, must be integrated from

$$p = \sqrt[4]{\frac{2A}{mV^2}}$$

to infinity. To evaluate these integrals, a few transformations must be made to get p in terms of k. From what has gone before,

$$p^2 = \frac{\left(b^2 + \frac{2mV^2}{b^2A}\right)}{\frac{2mV^2}{A}}, \text{ and } k^2 = \frac{Ab^4}{2mV^2}.$$

Thus
$$p^2 = \frac{(1 + k^2)}{k}\sqrt{\frac{A}{2mV^2}},$$

and $2\pi p dp = \pi\left(1 - \frac{1}{k^2}\right)\sqrt{\frac{A}{2mV^2}}dk$. Thus for the apsidal energy changes (*i.e.*, non-impact transfers), the energy loss E_1 is

$$E_1 = \frac{4M_1M_2}{(M_1 + M_2)^2}TN\pi\left(\frac{A}{2mV^2}\right)^{1/2}\int_0^1 (1 - k^{1/2})\cos^2\{(1 + k^2)^{1/2}F(k)\}dk,$$

for, while p goes from $\sqrt[4]{\frac{2A}{mV^2}}$ to infinity, k goes from 0 to 1. This follows since

$$p^2 = \sqrt{\frac{2A}{mV^2}} = \frac{k^2 + 1}{k}\sqrt{\frac{A}{2mV^2}} \text{ and if}$$

$\frac{k^2 + 1}{k} = 2$ and $k = 1$, and if $p = \infty$, $\sqrt{\frac{k^2 + 1}{k}} = \infty$ and $k = 0$.

Thus $$E_1 = 0.2\left\{\frac{4M_1M_2}{(M_1 + M_2)^2}TN\pi\left(\frac{A}{2mV^2}\right)^{1/2}\right\}.$$

For the impacts from $p = 0$ to $p = \sqrt[4]{\frac{2A}{mV^2}}$ reversal of direction takes place, $2\theta = \pi$, and $\sin\theta = 1$. This gives E_2, the impact loss, as

$$E_2 = (1)\frac{4M_1M_2}{(M_1 + M_2)^2}TN\pi\left(\frac{2A}{mV^2}\right)^{1/2}$$

on integration. The total loss of energy per cm path is $E_L = E_1 + E_2$, and this is

$$E_L = 1.1\frac{4M_1M_2}{(M_1 + M_2)^2}TN\pi\left(\frac{2A}{mV^2}\right)^{1/2}.$$

It may be pointed out here that the 0.1 factor in the energy loss due to apsidal exchanges is the fraction neglected by Wellisch and makes a correction of 10 per cent in his theory necessary. The above expression for E_L is the energy loss for a charged ion. Had the ion been uncharged and the impacts been between spheres, the energy loss would have been different. It can be computed as follows: Let s be the sum of the radii of ion and molecule, and p the perpendicular distance of the ion on the direction of motion of the molecule. In Fig. 69, since

$$2\theta = \pi - 2\alpha$$

$$\theta = \frac{\pi}{2} - \alpha$$

$$\beta = \pi - \frac{\pi}{2} - \alpha = \frac{\pi}{2} - \alpha.$$

Hence, $$\beta = \theta.$$

Therefore, $$\sin\theta = \sqrt{\frac{s^2 - p^2}{s^2}},$$

and $$\sin^2\theta = \frac{s^2 - p^2}{s^2}.$$

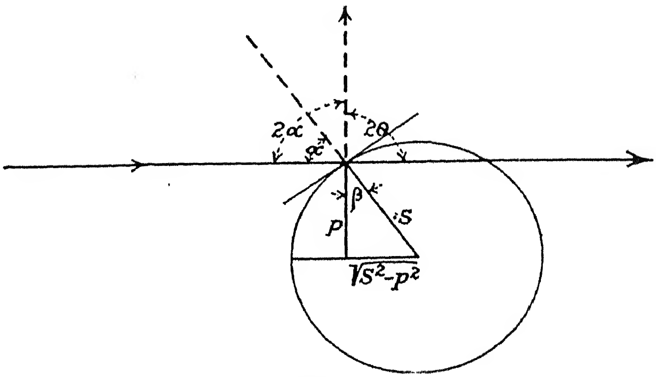

FIG. 69.

The energy loss would, then, have been E_E.

$$E_E = \frac{4M_1M_2}{(M_1 + M_2)^2}T\int_0^s \sin^2\theta N 2\pi p\,dp$$
$$= \frac{4M_1M_2}{(M_1 + M_2)^2}T\left(\frac{1}{2}N\pi s^2\right).$$

The ratio of energy loss per cm with the ions which attract molecules and the forceless ions which collide elastically would be

$$\frac{E_E}{E_L} = \frac{1}{2.2\left(\frac{2A}{mV^2s^4}\right)^{1/2}}.$$

In the derivation of the Langevin equation for elastic impacts, the equation set up for the case of equilibrium of the ion in the field (*i.e.*, a steady velocity of drift) equated the force due to the electric field to the rate of loss of momentum in impacts of the elastic solid type in the form,

$$K = \frac{mM}{m + M}\int\int(u - U)N\pi s^2 c\,df\,dF,$$

which on integration yielded

$$K = \frac{4\omega}{3}\pi N s^2\sqrt{\frac{4}{h\pi}\frac{mM}{m + M}}.$$

Now this loss of energy was that computed under E_E above. Assuming losses such as J. J. Thomson does, the rate of loss of energy is increased in the ratio

$$\frac{E_E}{E_L} = \frac{1}{2.2\left(\frac{2A}{mV^2s^4}\right)^{1/2}},$$

that is, the mobility equation of Langevin assuming forces, and assuming that these can be taken into account after the integrations above have been performed, leads to the transformed expression for K:

$$K = \frac{4\omega}{3}N\pi s^2\sqrt{\frac{4}{h\pi}\frac{mM}{m+M}}\,2.2\left(\frac{2A}{mV^2s^4}\right)^{1/2},$$

for the quantity E_E must be replaced by E_L and $E_L = E_E\,2.2\left(\frac{2A}{mV^2S^4}\right)^{1/2}$. Solving for ω and transforming K for the force produced by the field, the equation after reduction to terms of k, the mobility (see Sec. 105), becomes

$$k = 0.815\frac{e}{M}\frac{\lambda}{C}\frac{1}{2.2\left(\frac{2A}{mV^2s^4}\right)^{1/2}}\sqrt{\frac{m+M}{m}}.$$

Now $A = \frac{(D-1)e^2}{2\pi n}$, $m = \frac{M_1M_2}{M_1+M_2}$, and V is the relative velocity of ion and molecule.

Thus
$$\frac{1}{2}\frac{M_1M_2}{M_1+M_2} = \frac{1}{2}MC^2,$$

the energy of thermal agitation of the molecules. Hence k, the mobility, is

$$k = \frac{0.815e}{M}\frac{\lambda}{C}\frac{\sqrt{\frac{M+m}{m}}}{2.2\left\{\frac{(D-1)e^2}{\pi n s^4 MC^2}\right\}^{1/2}}.$$

If
$$\lambda = \frac{1}{\pi s^2 n},$$

then
$$k = \frac{0.815\sqrt{\frac{M+m}{m}}}{2.2\left\{\frac{nM(D-1)}{\pi}\right\}^{1/2}}.$$

Now $n = \frac{\rho}{\rho_o}N$, where N is the number of molecules per cm³ at $N.T.P.$, ρ_o is the density at $N.T.P.$, and ρ is the density corresponding to n. Also $D - 1$ varies with ρ; so that $\frac{\rho}{\rho_o}(D-1)_o = (D - 1)$, where $(D - 1)_o$ is $D - 1$ at a density ρ_o. Further, one can write $M = M_o\mu$, where M_o is the molecular weight, and μ the mass of an atom of hydrogen. Thus k is given by

$$k = \frac{0.815\sqrt{\pi}}{2.2(N\mu)^{1/2}} \frac{\sqrt{\dfrac{M+m}{m}}}{\dfrac{\rho}{\rho_o}\sqrt{(D-1)_o M_o}}.$$

The constant term takes the value 0.104 and k is thus

$$k = \frac{0.104\sqrt{\dfrac{M+m}{m}}}{\dfrac{\rho}{\rho_o}\sqrt{(D-1)_o M_o}}.$$

This is the equation deduced by Loeb,[29] from Thomson's equation of the energy loss. Its interest lies in that it gives k without any arbitrary assumptions as to cluster size, except for the influence of the mass factor $\sqrt{\frac{M+m}{m}}$. The latter changes only from 1.4 to 1 for the change from a small ion to an infinitely heavy cluster. The values given by it are of the correct order of magnitude and vary from substance to substance in fair accord with observation. A similar equation follows as a special case of the most complete mobility equation deduced, that of Langevin[31] for the case of only force field impacts with no impacts of the solid elastic type. The constant of the special case of Langevin's general equation, however, is different and the equation reads

$$k = \frac{0.235\sqrt{\dfrac{M+m}{m}}}{\dfrac{\rho}{\rho_o}\sqrt{(D-1)_o M_o}}.$$

The mobility outside of the mass factor is independent of e, it is independent of the assumed value of s, of λ, and of $\bar{c}$, or the temperature. It varies, however, as $\frac{\rho_o}{\rho}$, and as the $\frac{1}{\sqrt{(D-1)_o}}$

and $\frac{1}{\sqrt{M_o}}$. Experimentally, the nearly complete independence of temperature and of field strength had always surprised observers. The independence of the charge cannot be verified at present, although, if the explanation of some abnormally high mobilities of newly formed ThD ions by Erikson[13] as being due to double charges is correct, the theory fails. The variation of k as $\frac{\rho_o}{\rho}$ is one of the well-established facts about ionic mobilities. The variation of k as $\frac{1}{\sqrt{(D-1)_o M_o}}$, that is, inversely as the square root of the dielectric constant less unity multiplied by the molecular weight, is, in rough agreement with an old rule about ionic mobilities. Kaufmann[15] stated that k varied as $\frac{1}{\sqrt{M_o}}$ for the "permanent" gases, that is, for gases of about the same and rather low values of $D - 1$. Loeb,[32] in 1917, showed that it held more generally in the form that k was proportional to $\frac{1}{\sqrt{M_o}}$ multiplied by $\frac{1}{\sqrt[4]{(D-1)_o}}$. The fair agreement of k computed from the new relation k proportional to $\frac{1}{\sqrt{(D-1)_o M_o}}$ with experimental values is a sufficient test of the new theory. It, however, runs against a serious difficulty brought to bear against all mobility equations. k should vary as $\sqrt{\frac{M+m}{m}}$. Now experiments made on ThD[26] ions in air and in H_2 show that these ions have the same k as ions of H_2 in H_2 gas. Later experiments of Tyndall and Grindley[33] show that this holds for analogous cases within 1 per cent. This means that, while the ion theories demand a variation of at least a few per cent (about 12 per cent), with the mass of the nucleus of the ion, experiment shows less than 1 per cent variation. The difficulty is particularly severe for the above theory for the following reason: Erikson[34] finds that newly formed positive ions change from the value of the negative mobility which they initially possess to the lower value characteristic of positive ions in several hundredths of a second. The only explanation this theory could give of Erikson's results would be by the aid of the mass factor above. Other theories permit a change in s

due to clustering to account for the change. This theory assumes that the ionic mobility is insensitive to any change in s. Thus one is forced to mistrust somewhat the striking success of the equation. The failure is doubtless due to the inaccuracy of Thomson's assumptions as to path reversal at non-apsidal impacts. The equation has served one more useful purpose: It showed that with the absence of elastic solid impacts, except for the small mass factor, the mobility was not affected by the existence of the cluster. It therefore showed that, if the assumptions were correct, measurements of mobilities in pure gases should be "ignorant" of whether the ion was a cluster or not, thus showing a possible way out of the decade-long discussion of cluster-ion versus small-ion theories.

A further comment might be made on the independence indicated by theory and the still greater independence of the ionic mobilities of the mass factor. This, on the kinetic theory, receives a partial explanation, for, while a greater inertia slows up an ion, its increased persistence of the velocity gained in the field makes the mobility nearly independent of the mass. This can be seen from the Langevin deduction where the persistence was introduced giving the factor $\sqrt{\frac{M+m}{m}}$. The *complete independence* observed is not, however, explained by this.

The theory outlined above, while apparently satisfactory, as has been stated, runs against certain difficulties. These are the following: (1) If Erikson's conclusion about the nature of the very fast newly formed ThD ion is correct, the mobility is not independent of the charge. (2) If Tyndall and Grindley's[33] measurements are correct, which seems to be the case, the mass factor $\sqrt{\frac{m+M}{m}}$ may not be called on to explain the Erikson[34] ageing effect. Thus this must be explained as Erikson does on the change in the value of s due to the formation of a cluster ion. Erikson interprets his results by assuming that the negative ion is a single molecule while the positive ion changes from an initial single molecule to a bimolecular ion on ageing. Thus the radius of the ion must enter in. These two conditions are met if the elastic solid type of impacts be assumed to take place even to a limited extent. The result obtained theoretically was due to the *neglect of elastic solid type of impacts in the assumption of Thomson that all non-apsidal impacts result in the reversal of*

velocities (*i.e.*, are central). That this is incorrect may be shown by calculation of the value of p from the law of force. The value of p for non-apsidal distances for molecules of the gases is not more than two to four times the value of the molecular radius. Thus, for He, H_2, N_2, and HCl, p is, respectively, 3.65×10^{-8}, 5.02×10^{-8}, 6.12×10^{-8}, and 9.2×10^{-8} cm. For these same gases s is 2.18×10^{-8}, 2.47×10^{-8}, 3.5×10^{-8}, and 2.0×10^{-8} cm for a monomolecular ion and a molecule in contact. Accordingly, it is not surprising that the theory fails, for the impact occurs before the direction of motion of the molecule can come along the line of centers were it to do so ultimately.

109. The More Complete Equations and the Nature of the Ion. Another set of data[11] have come to light recently which show without question that clustering of a labile sort must occur in certain gases. The mobilities of ions in mixtures of gases should be given as a function of the percentage composition of the mixture by the simple relation

$$K_c = \frac{100K_AK_B}{(100 - c)K_B + cK_A}.$$

Here K_c is the mobility in the mixture of c per cent of gas B, and K_A and K_B are the mobilities in the pure gases. This was found in 1908 by Blanc[35] to be true for mixtures of the gases CO_2, air, and H_2. It had been observed by Wellisch and others that in certain other gases the mobility was lowered abnormally by the presence of certain vapors (*e.g.*, water vapor), while in others this was not so.[32] No quantitative data were, however, taken to back up this claim and the matter rested there. In an endeavor to settle the question of the nature of gaseous ions, Loeb[36] and Ashley in 1924 measured mobilities of ions in mixtures of NH_3 and air. It was expected that in a gas of such a high dielectric constant as NH_3, if clustering took place, the introduction of small traces of NH_3 would reduce the mobility abnormally due to the preferential attachment of the active NH_3 molecules to the ion. The result of these measurements was not as definite as expected. The mobility in the mixture was found to be given by a law of the form

$$K_c = \frac{K_AK_B}{\sqrt{\dfrac{(100 - c)K^2_B + cK^2_A}{100}}};$$

where c is the percentage of gas B in the mixture, and K_A and K_B are the mobilities in the pure gases A and B. The

significance of this was pointed out by Debye in a conversation. It indicates that the density of the NH_3 molecules in the neighborhood of the ion is greater than in the rest of the gas. Such an increased density can be considered as a sort of a statistical cluster. An extension of the measurements to HCl gas and air mixtures, however, yielded a still more striking confirmation of this assumption. While the mobilities obeyed the former law fairly well at high concentrations of HCl the mobility in HCl dropped by more than 20 per cent on the addition of a millimeter or two partial pressure of HCl. In fact, the observed mobilities were lower than those computed on the formula above until the percentage of HCl present was 20 per cent. This indicates very definitely a preferential clustering of HCl molecules about the ion. On the law of force between ions and molecules assumed above, the change in composition of the gas at various distances from the ion can be easily computed on the kinetic theory. This was done for HCl by Condon. Assume the gas made up of two kinds of molecules A and B. The density of the two kinds N_A and N_B is given in a field of force by the Boltzmann form of the distribution law. This says that $N_A = N_{Ao}e^{-\frac{E_A}{kT}}$, and $N_B = N_{Bo}e^{-\frac{E_B}{kT}}$.* Here k is the Boltzmann constant and T the absolute temperature, and E_A and E_B are the potential energies of the molecules at the place where their concentrations N_A and N_B are sought. N_{Ao} and N_{Bo} are the densities at a point so far from the force center that the composition is that of the average mixture. If the forces are given by $\frac{K_A}{r^5}$ and $\frac{K_B}{r^5}$, the potential energies at a distance r are $E_A = -\frac{K_A}{4r^4}$ and $E_B = -\frac{K_B}{4r^4}$. Thus one may write

$$\frac{N_A}{N_B} = \frac{N_{Ao}}{N_{Bo}} e^{\left(\frac{K_A - K_B}{4r^4kT}\right)}.$$

Also K_A and K_B are given by $K_A = \frac{(D_A - 1)e^2}{2\pi N_o}$ and $K_B = \frac{(D_B - 1)e^2}{2\pi N_o}$, where the significance of the symbols is that given in the earlier part of the chapter. Taking $D_B - 1$ for air as 0.00059, and the value for $D_A - 1$ for HCl at room temperature given by Zahn[37] as 0.0041, the ratios of the numbers of molecules

* This equation is discussed in the latter part of Sec. 36.

of HCl and air in any initial mixture of HCl and air at a distance r from the ion can be found from the relation

$$\frac{\dfrac{N_A}{N_B}}{\dfrac{N_{Ao}}{N_{Bo}}} = e^{\frac{(D_A - D_B)}{4r^4kT}} = e^{\frac{2.83 \times 10^{-29}}{r^4}},$$

if $N_o = 2.7 \times 10^{19}$, T is the absolute temperature, and k is the Boltzmann constant. This yields the values given below for

$$\frac{\dfrac{N_A}{N_B}}{\dfrac{N_{Ao}}{N_{Bo}}}.$$

r IN CM	$\frac{N_A/N_B}{N_{Ao}/N_{Bo}}$
1.14×10^{-8}	10^{700}
4.0×10^{-8}	545
5.74×10^{-8}	13.5
6.9×10^{-8}	3.4
8.0×10^{-8}	2.34
9.2×10^{-8}	1.48
1.14×10^{-7}	1.17
1.38×10^{-7}	1.08
1.14×10^{-6}	1.000016
1.14×10^{-5}	1.00000000

It is thus seen that the molecules that find themselves at the surface of a cluster ion of 4.6×10^{-8}-cm radius are HCl molecules in the ratio of 545 to 1 if the mixture contains 50 per cent HCl gas and air. In a mixture of 0.2 per cent HCl and 99.8 per cent air such a cluster would, on the average, consist of one HCl molecule to one air molecule. At greater distances from the ion the changes in concentration would be less striking and at the distance of one mean free path or at or 10^{-5} cm, in a 50 per cent HCl air mixture, there would be virtually no change in the concentration of the molecules due to the ion. In a homogeneous gas the mobilities of the ions on Thomson's theory are chiefly influenced by those molecules which come close enough to the ion to have their motion appreciably altered by its field of force. In a mixture, the molecules of higher dielectric constant (that is, those of greater activity on the ion), are, as seen above, present in far greater numbers in the immediate neighborhood of the ion

than in the rest of the gas. Thus they are disproportionately active in altering the mobility of the ion in the gas. The effect of the increased concentration of the active molecules in the neighborhood of the ion is not included in the mobility equation deduced above, for here the constitution of the gas was supposed to be uniform. The conclusion from the foregoing discussion is that a statistical clustering effect certainly takes place. To what extent the clustering is permanent, that is, to what extent the molecules stay permanently attached to the ion, the equation does not say. These indications make it seem wise to include in a proper ion theory the effect of the size of the ion, and to assume elastic solid impacts of a non-central type as a source of some of the energy loss experienced by the ion in the field.

Perhaps two attempts in this direction are worthy of note. The one was due to Sutherland,[25] who used a type analysis which was characteristic of his treatment of the variation of the coefficient of viscosity with temperature (see Sec. 62). The analysis for which there is no place here led him to an expression for the change of the ionic mobility with temperature. This reads $k = \dfrac{A^{1/2}}{1 + \dfrac{c}{T}}$, where A and c are constants, and T is the absolute temperature. The equation was in agreement with Phillips'[39] results made at constant pressure. These results are, however, in disagreement with those of Kovarick[38] at constant pressure and with those of Erikson[10] at constant density, so that the agreement may be meaningless. From the constants A and c put in his full mobility equation and assuming a *small molecular ion*, Sutherland computed mobilities about 9.6 times as great as those observed. This makes his equation rather arbitrary, as it requires an assumed added electrical friction of 8.6 times the kinetic friction to make the results agree.

The second theory mentioned, which is doubtless the most satisfactory theory possible to deduce with the present knowledge of the law of force between ion and molecule, is due to Langevin.[31] In this theory Langevin deduces the mobility of a spherical ion of variable radius, suffering elastic solid impacts with molecules considered spherical, at the same time exerting forces on them which vary as the inverse fifth power of the distance. The analysis is as rigorous from the kinetic-theory point of view as is possible with the methods available. It is too long to reproduce

in this text and the reader must obtain it from the original article. It leads to an expression for the mobility of the ion of the form

$$k = \frac{3}{16Y} \frac{\sqrt{\dfrac{M + m}{m}}}{\dfrac{\rho}{\rho_o}\sqrt{(D - 1)_o M_o}}.$$

Here the second member of the equation is the familiar one given by Loeb (Sec. 108), in which the mobility depends on the dielectric constant D_o and the molecular weight M_o only. The quantity Y is, however, a complex function of μ given by

$$\mu = \sqrt{\frac{3(D - 1)_o e^2}{4\pi N_o s^4 MC^2}}.$$

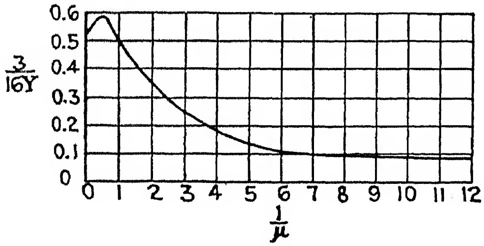

FIG. 70.

This may be evaluated in terms of the graph of Fig. 70, where $\frac{1}{\mu}$ is plotted as abscissæ against Y as ordinates. When μ has very large values and $\frac{1}{\mu}$ approaches 0, it is seen that $\frac{3}{16Y}$ takes on a value 0.505, that is, when s becomes small, $(D - 1)_o$ large, or the temperature MC^2 is low, the equation takes on a form in which the Thomson equation assumed by Loeb gives the correct results. In general, this is not true and μ has moderate values. Thus the special case is modified to take account of the elastic solid impacts. It is perhaps the best equation which there is for ionic mobilities (see Hassé[40]). It does contain an arbitrary factor s depending on the ionic radius. The influence of this is, however, not supreme. It is seen that μ here, and hence k, also depend on the charge e.

In order to compare the values of k derived from these various equations, a table computed by A. M. Cravath is given below. The mobilities in certain gases are recorded as observed experi-

mentally. Then follow the values of k computed on two assumptions, making the two parts of the table. The first set of values are computed assuming that the ion is a single molecule, the second, that the ion is a cluster of 12 molecules about a central charged molecule. The number 12 was chosen, as it is the greatest number of spheres that can be packed about a single sphere of equal radius. As can be seen from the foregoing, the latter is perhaps an overestimate of the size of the ion, while the former is an underestimate, at least for the positive ions. To show the effect of the mass factor, the mobility of a charged H_2 molecule in a heavier gas is computed on these theories. As is seen, all of them demand a higher mobility of the H_2 ion than for the ions of the given gas in the gas. Experimentally, this is not observed to be the case, and it argues strongly for a clustering.

PART 1.—SMALL MOLECULAR ION

Observed			Langevin elastic impacts	Corrected Wellisch	Loeb forces alone acting	Complete Langevin forces and elastic impacts
Gas	+ Ions	− Ions				
Air	1.4	1.8	9.85	2.08	1.12	3.17
H_2	6.02	7.68	67.5	9.90	6.21	17.3
HCl	0.65	0.56	4.47	0.58	0.382	1.08
Ether	0.19	0.22	2.56	0.294	0.208	0.565
H_2 ions in air	1.4	1.8	35.9	4.82	3.09	8.70

PART 2.—CLUSTER OF 12 MOLECULES

Observed			Langevin elastic impacts	Corrected Wellisch	Loeb forces alone acting	Complete Langevin forces and elastic impacts
Gas	+ Ions	− Ions				
Air	1.4	1.8	1.80	1.46	0.822	1.63
H_2	6.02	7.68	12.3	9.08	4.60	10.23
HCl	0.65	0.56	0.817	0.582	0.280	0.657
Ether	0.19	0.22	0.468	0.318	0.153	0.363

Although the mobility equation of Langevin seems to fit the conditions observed fairly well, there are two things that no ion theory can do. In the first place, the theories are all incapable

quantitatively of accounting for the independence of mobility and mass of the nucleus to within 1 per cent as observed by Tyndall and Grindley.[33] They are, furthermore, incapable of distinguishing quantitatively between the mobilities of positive and negative ions.* This lies in the assumption of the force factor in the attractive law of force assumed $\left(i.e., \text{ the } \frac{(D-1)_o e^2}{2\pi N_o}\right)$ being independent of the sign of the charge. In bulk, where the dielectric displacements are measured in uniform fields of force, the molecules behave equally to positive and negative poles. On the other hand, in the field of force of an ion the field acting on a molecule within a distance s from the center of a charged molecule is not uniform. Thus, the side of the molecule nearer the ion is in a far stronger field of force than that away. Also, other considerations must enter in. The molecule is predominantly electrically negative at its surface, for the electrons describe orbits over the surfaces of the molecules, while the positive charges are near the center. When ion and molecule are close together, the force of the charge of the ion is more intense on the surface of the molecule (which is nearer) than on its center. If the ion is negative, the greater force on the molecule is the negative repulsion of the surface electrons of the molecule, while if the ion is positive, the greater force is the attraction of the ion on the negative surface of the molecule. While these differences may not be large, they would easily give a sufficient difference in attraction to account for the difference in k. At a relatively small distance between ion and molecule as one recedes from the ion, these differences would practically vanish. Thus, while k for the ions is decreased, in the main, by the same large amount due to dielectric attractions depending on $(D-1)_o$, on close approach there is a difference in the force which causes the molecules to be attracted slightly more to the positive ion than to the negative ion. Hence, in general, it would be expected that the positive ion has a lower k than the negative ion. This is the case.

For gases with higher D and for gases with large molecules, the positive and negative mobilities are more nearly the same.

* This is not quite correct, for Hassé has recently (*Phil. Mag.*, **1,** 139, 1926) computed the positive and negative mobilities, assuming that the former was a monomolecular layer about a positive molecule and the latter was a monomolecular layer about an electron using the Langevin theory. While the values obtained are of the proper order of magnitude, the electron attachment results speak against it as does Loeb's work in HCl gas.

Finally, in HCl and in H_2O and H_2S the negative ions are less mobile than the positive ions. Condon explains this on the fact that in HCl the electrons are chiefly about the Cl atom. The H atom with its positive charge is free, or at least near the surface of the molecule. In such an arrangement the orientation of an HCl moelcule in the radial field of a negative ion will be with the H atom toward the ion. The forces will be relatively intense in such a case. In the field of a positive ion the orientation would be reversed, and while the outer electrons of the molecule would be displaced towards the positive ion the force would be less than on a molecule which had no free H atom with a positive charge pulling the Cl electrons the other way. Thus in HCl the negative ion attracts the molecules more strongly than the positive ion does. Accordingly, the mobility of the negative ion is less than that of the positive ion. The case should be the same in water and H_2S, where it is observed that water vapor depresses the negative-ion mobility more than it does the positive-ion mobility. Also, the recent theoretical work of Hund[41] shows that the hydrogen nuclei in these molecules are so placed as to be on one side and near the surface. For vapors like alcohol, where the OH group can also show this effect, the result will be more or less of a compromise between the two types of action. The result will be that, in general, the negative and positive mobilities will be nearly equal. It is thus seen that, by a more minute consideration of the action between ions and molecules, the difference in the mobility of the ions of opposite sign can be qualitatively accounted for. Quantitatively, this is out of the question until the laws of force become established. Until then, therefore, very little further progress can be made towards a better ionic mobility equation.

110. The Coefficient of Recombination of Ions.—If a gas be ionized and then left to itself, the forces between the positive and negative ions will cause them gradually to drift together. As they do this, they neutralize their charges and the ions disappear from the gas. If the ions are present in equal numbers and are distributed at random, it seems reasonable to write that $\frac{dn}{dt} = -\alpha n^2$, where n is the number of positive or negative ions present per cm³ and dn is the change in number of the ions in a cm³ in unit time. This equation, when integrated, has been tested experimentally and seems to hold for some cases of ionization.

For the case of ionization by α particles, where the ionization is restricted to regions close to the paths of the α particles, Bragg and Kleeman[42] have shown that the law does not hold. It is even questionable whether it holds for X-ray ionization, for, in general, the electrons liberated do not move far away from the parent molecules. That it effectively holds is, however, attested by the fact that deductions based on the assumption agree fairly well with experiment. As will be seen later, there may be reason to doubt its entire validity in later stages of recombination. This will be seen from a study of the mechanism of recombinations. Perhaps the time range over which the equation has been tested has been so relatively short that the results are not significant.

The constant α is a characteristic of the gas and requires evaluation on the basis of the kinetic theory. One treatment of the problem is given by Langevin.[43] This, with an added consideration by Richardson,[44] leads to one of the interesting theories. More recently, J. J. Thomson[45] has derived an expression for α which independently incorporates the idea of Richardson. While perhaps it is less rigorous than that of Langevin, the equation is in better agreement with facts. In this equation the loss of rigor is due to his failure to include the action of the attractive forces between the ions. As the change in α produced by these is small, the error is not great.

Langevin proceeds as follows: Assuming that 10^6 or 10^7 ions are generated in a cm^3 of gas, the average distance between them is about 10^{-2} cm. The field of one ion at the other is then about 1.4×10^{-4} volts/cm (that is, it is very weak). When the ions are at 10^{-4} cm apart, or separated by about 10 free paths, the field is about 14 volts/cm and the ions begin to approach each other with a greater speed. At the distance of a free path, the field is of the order of 1400 volts per cm and the ions rush towards each other. Now with these speeds superposed on their velocities of thermal agitations, it turns out that the relative kinetic energies are greater than their potential energies at closest approach. They will then describe hyperbolic orbits separating again. If the one ion should collide with a molecule in the immediate vicinity of the other ion, it might lose the excess kinetic energy to the molecule. Thus it would not be able to leave the vicinity of the ion attracting it, and the pair would describe closed orbits about their common center of gravity until the excess electron of the negative ion hopped across to the

positive ion, radiated its energy, and the two separated as neutral molecules. Accordingly, the process of recombination consists essentially of three periods: first, the period of coming to within a free path of each other; second, the period of describing orbits of the hyperbolic types until the excess kinetic energy derived from the potential energy of their attraction and separation is dissipated; and, third, the period of electron transfer, at which, while the ions would act outwardly neutral, they could be separated by the heat impact of a neutral molecule. For this discussion it will be assumed that the recombination is complete while the third step is taking place, although this may not be true. If the period of coming together is relatively great, this largely determines α. Under this condition, the alterations in distribution of ions with time would exert relatively little influence on the recombination and one would expect α to follow laws which demand a random distribution of ions throughout. As will later be seen, the second period is not always insignificant, and with electrons it might be the controlling factor. Thus both periods are of importance and it is essential that the fundamental equation defining α be tested to make sure that the distribution in later phases of the recombination does not materially alter the equation and hence influence α.

To derive the meaning of α, Langevin uses an exceedingly ingenious concept to simplify the considerations. Imagine an ion fixed and the other ion moving towards it. The field acting on the moving ion is always towards the fixed ion as long as no other ion is in the neighborhood. Its intensity is, furthermore, given by $\frac{4\pi e}{r^2}$, where r is the distance between them. Since the relative velocity is the sum of the mobilities multiplied by the field strength, then the velocity of approach is $4\pi\frac{e}{r^2}(K_+ + K_-)$. If each charge that is fixed be surrounded by a spherical surface of varying radius r, then it is clear that the number of ions moving through each such surface towards the other ion under their forces of attraction is independent of the radius of the surface, that is, since the velocity is proportional to $\frac{1}{r^2}$, and the surface varies as r^2, the number moving through the surface which depends only on a product of these two and the density of the ions is independent of r and hence of the size of

the surface. Thus if a surface be chosen small enough, the number of ions of one sign diffusing through such surfaces about ions of the other sign per unit time will give the rate of recombination of the ions.

To carry on the rigorous analysis, Langevin chooses an element of volume about each ion so small, compared to the average distance between ions, that the chance of more than one ion of opposite sign moving through the surface at any one time is small. This insures that the field is proportional to $\frac{1}{r^2}$. From the considerations above, this could be a volume of radius one-tenth the average distance between ions. It is also necessary to show that the motions of the ions towards each other due to the charges is the predominating action. Otherwise the velocity again would not be $\frac{e}{r^2}$. To do this Langevin believes that he shows that recombination due to heat motion is a small fraction of the observed value. In this he may be incorrect, as Thomson's equation shows. Each negative ion may then be considered surrounded by a surface S as above. It is required to find how many positive ions pass in a time dt into the interior of all these surfaces due to the attraction of the negative ions. As was shown before, this number will define the number of collisions between ions of opposite sign, in the time dt, which is the important phase of the first period in recombination. The ions move with velocities towards each other determined by the field $\frac{e^2}{r^2}$ of the ions and their mobilities K_+ and K_-. Let n_+ and n_- be the numbers of ions of opposite signs per cm³. In the volume $d\nu$ of surface S there will be $n_- d\nu$ and $n_+ d\nu$ ions. The question then arises as to how many of these positive ions penetrate into the negative volumes through a surface dS during dt. This depends only on the relative velocity of the central ion and the positive ion near dS. The velocity of the negative ion is $V_- = -K_- \frac{e}{r^2}$ and that of the positive ion is $V_+ = K_+ \frac{e}{r^2}$. The relative velocity V is $(K_+ + K_-)\frac{e}{r^2}$. The ions that pass through dS in dt are in a cylinder having dS for base and of length Vdt parallel to V. If V_n is the projection of V on the normal to dS, the volume is

$V_n dS dt$. For all the $n_- d\nu$ surfaces in the volume $d\nu$ the total volume of these cylinders swept out will be represented by

$$\sum V_n dS dt.$$

For the n_+ ions/cm³ the number of positive ions lying in this volume is, therefore,

$$n_+ \sum V_n dS dt.$$

Integrating with respect to dS,

$$n_+ dt \sum \int_s V_n dS.$$

Now the latter integral can be represented by

$$\int (K_+ + K_-) \left(\frac{e}{r^2}\right)_n dS,$$

where $\left(\frac{e}{r^2}\right)_n$ is the normal flux through dS. Further, dS is part of the surface of the volume $d\nu$ drawn about the negative ions. In polar coordinates $dS = r d\theta r \cos \theta d\phi$.
Thus,

$$n_+ dt \sum \int_s V_n dS$$

$$= n_+ dt \sum (K_+ + K_-) \int_{-\frac{\pi}{2}}^{+\frac{\pi}{2}} \int_0^{2\pi} \frac{r^2 e}{r^2} \cos \theta d\theta d\phi,$$

$$= n_+ dt \sum e(K_+ + K_-) 4\pi.$$

After integrating, it is possible to replace the $\sum e(K_+ + K_-)4\pi$ by its equivalent $n_- d\nu e(K_+ + K_-)4\pi$, for the $n_- d\nu$ negative ions in the volume considered, that is, the number of positive ions that enter the cells of the negative ions in the volume $d\nu$ in dt is expressed by

$$n_+ dt \Sigma \int_s V_n dS = n_+ n_- dt 4\pi (K_+ + K_-) e d\nu.$$

If $d\nu$ be set equal to 1 cm.³, this gives the number of positive ions that enter the cells (that is, recombine with the negative ions in a cm³ of volume in dt. This number is $dn = -n_+ n_- dt 4\pi (K_+ + K_-)e$, where the $-$ sign denotes that n decreases as increases. Since, by definition,

$$\frac{dn}{dt} = -\alpha n_+ n_-,$$

then
$$\alpha = 4\pi (K_+ + K_-) e.$$

Thus α is merely $4\pi(K_- + K_+)e$. Evaluation of α and comparison to experiment, however, showed that the value of α taken from K_+ and K_- was too large as given by this equation. The α observed for most ions lies around $3400e$, where e is the electron, and the 3400 applies to a K in electrostatic units (that is, K in volt/cm multiplied by 300). As e is 4.77×10^{-10}, the observed $\alpha = 1.6 \times 10^{-6}$. The α computed for air from the above is 6.9×10^{-6}. Langevin, therefore, multiplied his value $4\pi(K_- + K_+)e$ by a quantity ϵ, which is a quantity less than unity, giving the fraction of collisions which end in recombination, for, instead of considering the second period mentioned in the Introduction, he assumed that, of the ions coming together, only a fraction recombine; the others separate and perhaps recombine with entirely different ions later. He devised methods of measuring ϵ which enable α to be computed. This leads to values of ϵ from 0.9 to 0.01, depending on the pressure of the gas and other factors. J. J. Thomson and O. W. Richardson independently calculate the value of ϵ on the hypothesis that, in order to recombine, one of the ions must strike a molecule and lose the energy gained in coming together in order to stay together. This calculation involves the second period in recombination. According to Richardson and Thomson, this would be characterized by a probability of recombination or escape. Here, again, the fraction that does not recombine is supposed to lead to complete separation of the two ions. As pointed out by A. M. Cravath, in a discussion of this subject the assumptions made by Richardson and Thomson may not lead to such a complete separation. In fact, the ions must remain relatively near each other and ultimately recombine. Before proceeding to the calculation of the factor ϵ, it is of interest to calculate the rate of recombination as Thomson does. This can be compared with Langevin's computation and the value of ϵ derived by Thomson may at once be applied to Langevin's equation.

Two ions separated by a distance r will separate to infinity when left to themselves in empty space if $\frac{1}{2}\frac{M_1M_2}{M_1 + M_2}(V_1^2 + V_2^2 - 2V_1V_2 \cos \theta)$ is greater than $\frac{\mu}{r}$, where M_1 and M_2 are the masses of the ions 1 and 2, V_1 and V_2 are their velocities, θ is the angle between their velocities, and $\frac{\mu}{r^2}$ is the force of attraction at r.

If the ions have a mean energy equal to their kinetic energy of agitation $\frac{1}{2}M_1V_1^2 = \frac{1}{2}M_2V_2^2 = \frac{3}{2}RT = \beta T$, where $\beta = 2.02 \times 10^{-16}$. If $\cos\theta$ has an average value of 0, the ions will separate if $\beta T > \frac{\mu}{r}$, that is, two ions can recombine only when they have the energy of thermal agitation if they are within a distance $r \leq \frac{\mu}{\beta T}$ of each other. The physical meaning of this is that, if the ions were initially infinitely far apart when left to themselves they would just escape from each other to infinity, that is, if one were fixed the other would describe a parabola about it returning to infinity. If, now, they had the velocity of thermal agitation superimposed, this would convert the orbits to hyperbolæ. Accordingly if while falling freely from some point nearer than infinity, an ion starting from rest would describe a closed orbit about its partner and hence recombine this could no longer happen with an ion starting from the same place with the energy of thermal agitation. In fact, with the heat motions of the ions, the energy of thermal agitation at a given r would have to be less than the energy gained by a free fall from infinity in order that recombination could occur. The distance r for this is, then, definitely the distance $\frac{\mu}{\beta T}$. At 273° abs. this distance is 4.18×10^{-6} cm, that is, about one-half a mean free path for air. Thus, for distances further than this from the ion, the thermal agitation is greater than the energy of free fall from infinity. Now in practice, the ions have the velocity of thermal agitation up to the point of their last collision with the molecules before coming together. Unless this last collision which causes them to lose the energy which they gained from the field over the last free path occurs within the sphere of radius $\frac{\mu}{\beta T}$ about the other ion, recombination at this approach will not occur. Thus recombination can only take place when the ions come together under conditions where one or the other has collided with a molecule within $\frac{\mu}{\beta T}$ of its companion. To get the recombination proceed as follows: Designate the ions of opposite sign as A and B particles. Describe about each A particle spheres of radii $\frac{\mu}{\beta T}$. The number of recombinations due to B particles will then be

counted as the number of collisions made by the B particles with neutral molecules inside these A spheres. The number of such collisions in unit time will be the rate of recombination due to B particles. Again, the A particles will have impacts with neutral molecules inside of the spheres $\frac{\mu}{\beta T}$ about the B particles, and the number of these per unit time give the rate of recombination due to A particles. The sum of these gives the rate of recombination of ions in the gas. Call d the radius of the spheres $\frac{\mu}{\beta T}$ about A and B. If the directions of motions of A and B particles are equally probable, the number of B particles passing through the spheres per second is merely the relative velocity of A and B molecules $\{U_A^2 + U_B^2\}^{1/2}$ times the area of the great circles of the spheres πd^2, multiplied by the density ρ' of the B particles, for $\pi d^2\{U_A^2 + U_B^2\}^{1/2}$ is the volume swept out per second, and ρ' times this gives the number of B particles that would lie in this volume. For the A particles passing though the B particle spheres, one has analogously

$$\pi d^2 \rho \{U_A^2 + U_B^2\}^{1/2}$$

where ρ is the number of A particles per cm³.

Now it becomes necessary to determine the number of collisions made by an ion in passing through such a sphere with the molecules in it. From the distribution of free paths (see Sec. 21), one has that the chance of an ion going x without an impact is $e^{-\frac{x}{\lambda'}}$, where λ' is an ionic free path in the gas. Now assume that, as the ion goes through a sphere of radius d about another ion, its path is not curved. How correct this assumption is may be seen from the value of d at 273°, which is 4.18×10^{-6} cm. It was shown that when the ion was one mean free path away from the other ion the field was 1400 volts per cm. Such a field would materially curve the path of the entering ion. This error must, therefore, be allowed for, but for simplicity the assumption may be made. If this straight path of the ion make an angle ψ with the normal to the surface of the sphere at the point where it enters, the length of the path is $2d \cos \psi$, as may be seen from Fig. 71. Since the chance of an angle ψ is $\frac{2(2\pi d \sin \psi \, (d\psi)d)}{4\pi d^2} = \sin \psi d\psi$ as seen in Fig. 71, the chance of crossing the sphere without an impact is

$$\int_0^{\frac{\pi}{2}} e^{-\frac{x}{\lambda'}} \sin\psi d\psi = \int_0^{\frac{\pi}{2}} e^{-\frac{2d\cos\psi}{\lambda'}} \sin\psi d\psi = \frac{\lambda'}{2d}\left(1 - e^{-\frac{2d}{\lambda'}}\right).$$

Thus the chance of an impact in the sphere is

$$\epsilon = 1 - \frac{\lambda'}{2d}\left(1 - e^{-\frac{2d}{\lambda'}}\right),$$

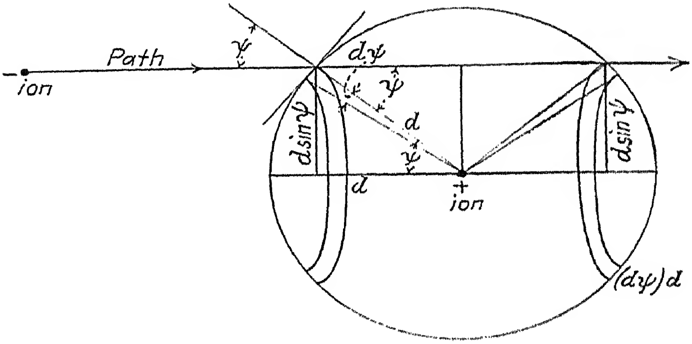

FIG. 71.

that is, out of a given number of encounters between ions the number recombining is ϵ times this. Thus, as Langevin computed the number in a time dt in dv as

$$dn_1 = n_+n_-4\pi(K_- + K_+)edtdv,$$

only ϵdn_1 of these recombine. Thus $dn = \epsilon dn_1$ and

$$dn = \epsilon n_+n_-4\pi(K_- + K_+)edtdv,$$

which leads to the Langevin-Richardson value of α_L as

$$\alpha_L = 4\pi(K_- + K_+)e\left[1 - \frac{\lambda'}{2d}\left(1 - e^{-\frac{2d}{\lambda'}}\right)\right].$$

In Thomson's deduction, one must multiply the recombinations due to B ions with gas molecules by the factor ϵ, which gives

$$dn_B = \rho\left[\pi d^2\rho'(U_A{}^2 + U_B{}^2)^{1/2}\left\{1 - \frac{\lambda'}{2d}\left(1 - e^{-\frac{2d}{\lambda'}}\right)\right\}\right]dt,$$

where ρ is the number of A molecules per cm³ and λ' is the free path of a B ion. Similarly for the A ions which collide with the ρ' B ions in a cm³, if the free path of the A ion is λ, then

$$dn_A = \pi d^2\rho\rho'\left[(U_A{}^2 + U_B{}^2)^{1/2}\left\{1 - \frac{\lambda}{2d}\left(1 - e^{-\frac{2d}{\lambda}}\right)\right\}\right]dt.$$

As

$$dn = -\alpha\rho\rho' dt,$$

Thomson's value of α, α_T, becomes

$$\alpha_T = \pi d^2(U_A{}^2 + U_B{}^2)^{1/2}\left\{1 - \frac{\lambda}{2d}\left(1 - e^{-\frac{2d}{\lambda}}\right) + 1 - \frac{\lambda'}{2d}\left(1 - e^{-\frac{2d}{\lambda'}}\right)\right\}.^*$$

Now

$$d = \frac{\mu}{\beta T} = \frac{e^2}{\beta T}, \text{ whence } d = 41.8 \times 10^{-6}\frac{273}{T}.$$

This d is constant with pressure but varies as $\frac{1}{T}$. For comparison, the Langevin equation for α with ϵ as computed above is

$$\alpha_L = 4\pi(K_+ + K_-)e\left\{1 - \frac{\lambda}{2d}\left(1 - e^{-\frac{2d}{\lambda}}\right)\right\},$$

where d has the value above, and λ is the free path of the ion. The factor ϵ therefore varies both with pressure and with temperature. The equations can be discussed in terms of two approximations of the function ϵ. This depends on the value of the ratio $\frac{\lambda}{d}$. d is comparable with λ for molecules at atmospheric pressure. For air molecules, λ at atmospheric pressure is 1.02×10^{-5} cm. Thus $\lambda = 2.5d$. For ions λ is about $\frac{1}{5}$, the value for air molecules, so that $\lambda = 0.5d$. For low pressures, $\frac{d}{\lambda}$ is small, and when this is so

$$1 - \frac{\lambda}{2d}\left(1 - e^{-\frac{2d}{\lambda}}\right) \doteq \frac{d}{\lambda}.$$

Hence at low pressures the α_T and α_L become

$$\alpha_T = 2\pi(U_A{}^2 + U_B{}^2)^{1/2}d^3\left(\frac{1}{\lambda} + \frac{1}{\lambda'}\right)$$

and

$$\alpha_L = 4\pi(K_+ + K_-)e\frac{d}{\lambda}.$$

When $\frac{2d}{\lambda}$ is large,

$$1 - \frac{\lambda}{2d}\left(1 - e^{-\frac{2d}{\lambda}}\right) \doteq 1,$$

* It should be pointed out here that this deduction assumes that ρ and ρ', the molecular density about the ions, are the same as in the rest of the gas. For a cluster ion, and particularly for an ion of the type as given in Sec. 109, this is not so and the factor ρ is increased by this fact. This should be included in these considerations.

whence α_T and α_L take on the values

$$\alpha_T = 2\pi(U_A^2 + U_B^2)^{1/2}\, d^2$$
$$\alpha_L = 4\pi(K_- + K_+)\epsilon.$$

At low pressures, as λ' and λ are inversely proportional to the pressure while d and U_A and U_B are independent of it, α_T *should vary as the pressure* p. The Langevin α_L has the ratio $\frac{K}{\lambda}$ in it. Now K varies inversely with pressure and so does λ, hence at low pressures Langevin's equation would lead one to *expect* α_L *independent of pressure.* Experimentally, at low pressures α varies with the pressure very rapidly according to Langevin. The quantity ϵ as measured by Langevin changes from 0.8 at 760 mm. to 0.01 at 152 mm. that is, much more rapidly than proportionally to p. As regards the value of α from Langevin's measurements, ϵ was computed from $\frac{\alpha}{4\pi(K_+ + K_-)\epsilon}$, which is assumed to vary as p. Hence α decreased by a factor of 16.1 in a change of pressure from 760 to 152. This is greater than that observed more recently by Thirkill,[46] who found α to decrease by a factor of 3.8 for a change in p from 760 to 196 mm. and also greater than the value observed by Hendren,[47] who found α to change by only 3.3 in a pressure change from 760 to 10 mm. of air. According to the theory of J. J. Thomson, ϵ, and accordingly α, should change in the ratio of $\frac{0.55}{0.18} = 3.04$ for change in pressure from 760 to 152 mm. if λ is assumed for an ion to be one-fifth that for an air molecule. The discrepancy of experimental results makes a more accurate comparison of theory and experiment impossible. The Thomson equation is, therefore, unquestionably better off in this respect than the Langevin equation as modified by Richardson, for the latter makes α_L independent of pressure. At high pressures the value of α_T should be nearly independent of pressure and ϵ should be near 1. Langevin and McClung also found that α was nearly constant at 5 atmospheres, and the values of ϵ computed lay above 0.9. The modified Langevin theory demands that α_L vary inversely as the pressure when ϵ is near unity. This is again in disagreement with facts. Thus, again, the Thomson theory which places the value of α on a velocity of thermal agitation instead of a recombination due to attraction appears to be more satisfactory. Again as regards the change in α with

temperature, ϵ is dependent on temperature to a small extent, for d is proportional to $\frac{1}{T}$. If density is constant, λ is independent of T, or nearly so. Also U_A and U_B are proportional to $T^{1/2}$ and K is nearly independent of T. Thus for *low pressures* α_T *should vary as* $T^{-5/2}$ and at *high pressures it should vary as* $T^{-3/2}$. *The* α_L *should vary as* T^{-1} *at low pressures,* while at *high pressures* α_L *should be independent of* T. As the temperature increases at constant density, Erikson[48] finds that α rapidly decreases. These measurements were made about 760 mm. In the range from 94 to 428° abs. Erikson found α to increase more than sixfold, while the $T^{-3/2}$ law demands a change in α by about a factor of 9. In this respect the Thomson theory again seems to have the advantage for it is only at *low pressures* that α_L should vary as T^{-1}.

The magnitude of α_T may be computed very easily. This depends on the velocities U_A and U_B, which depend on the mass of the ions, and it also depends on their mean free paths λ and λ'. If $U_A = U_B$ and $\lambda = \lambda'$, and if these are the same as for molecules of air, $U_A = 4.25 \times 10^4$ cm/sec., and $\lambda = 1.02 \times 10^{-5}$ cm, then one obtains for α_T the value 1.96×10^{-6} at 1 atmosphere, and at 5 atmospheres $\alpha_T = 6.5 \times 10^{-6}$. These values are in good agreement with those observed for air, which is 1.7×10^{-6} at 760-mm pressure. The Langevin expression α_L gave 2.1×10^{-5}. If this be multiplied by ϵ for air, assuming $\lambda = 1/5$, the λ for molecules in air $\epsilon = 0.75$ and $\alpha_L = 1.6 \times 10^{-5}$. The calculation for α_T as given by Thomson on the basis of air molecules is hardly correct, for the mass of the ion is certainly greater than that of the molecule. If the mass were four times as great, U_A would be one-half as great, and if λ were taken as $1/5$ the λ for molecules of air the ϵ factor in Thomson's equation would be 0.75 instead of 0.33, so that $\alpha_T = 2.2 \times 10^{-6}$, on this assumption. The change is, therefore, not very great, so that in this regard the theory of Thomson gives better values than does that of Langevin as modified by Richardson.

To overcome the latter discrepancy of the Langevin theory, Richardson suspected (probably correctly) that the velocity of the ion was not reduced to that of thermal agitation at *one impact* and decided that several impacts were needed to reduce the velocity. The probability of two, three, and more impacts inside the sphere of radius d were computed by Richardson and he then tested which value of ϵ_1, ϵ_2, ϵ_3, etc., computed for different

numbers of impacts, gave the best results. The value of ϵ which agreed well was given for the case of about three impacts, where $\epsilon = \left(1 + \frac{e^{-\frac{2d}{\lambda}}}{\frac{2d}{\lambda}}\right)(1 - e^{-\frac{d}{\lambda}})^2$. This, however, did not fit CO_2 except at low values for $\frac{d}{\lambda}$. While the idea is perhaps correct, it does not materially improve Langevin's equation. The neglect of the curvature of paths and of the cluster nature of the ion makes further speculations about ϵ of this nature rather futile. While the Thomson value for α seems to fulfil theoretical expectations fairly well, it is a fact that even this equation fails in another respect, as does the Langevin equation. The values of α in the gases, air, CO_2, and H_2 from the data of Townsend[49] are approximately 1.63×10^{-6}, 1.67×10^{-6}, and 1.49×10^{-6}. The values by other workers for these gases, while slightly different, are all in agreement in not assigning to ions in these gases radically different values of α. Now according to Thomson, α_T from these gases depends on $U_A = U_B$, and on ϵ. The values of U_A for H_2 relative to air, and for air relative to CO_2, are 3.8 and 1.24. The values of λ in these gases are in the ratio of $\frac{2}{1}$ and $\frac{1.5}{1}$. The quantity ϵ in these two cases is then changed in the ratio of $\frac{0.56}{0.75}$ and $\frac{0.9}{0.75}$. Thus the value of α_T for H_2 should be 6×10^{-6} and for CO_2 should be 2×10^{-6}. The observed values do not vary nearly as much with the change in gas, as the theory demands. The Langevin theory would require the same general variation, for the value of K in H_2 bears the ratio of about $\frac{6.4}{1.6}$ or $\frac{4}{1}$ to that in air, as was computed from the value of U_A. The insensitivity of the equations to the changes in U or K is caused by the fact that ϵ varies in the opposite sense with U and ϵ, for a larger U or K and a larger λ go together. Still the discrepancy of H_2 and air is striking enough.* It is possible that Townsend's values for α in H_2 are in error, so that the equation is correct. The theory needs a redetermination of α in H_2, in

* Recent work[11] shows that ions in impure H_2 may be made of heavier molecules. This would make U_A and U_B less and explain the result on Thomson's theory but not on Langevin's.

very pure gases, and with modern methods to test this point, for no other values of α in H_2 are extant.

If the discrepancy is a real one it requires explanation. One which has forced itself onto the stage in recent years is a suspicion first mentioned by Rümelin[50] that free electrons having a large K or U and a small λ may play a rôle. This becomes more probable in the light of the work of Loeb[17] and Wahlin[51] (to which reference will later be made), that electrons remain free in a gas for considerable periods of time. Thus with a K or a U a thousand times greater than for ions, the recombination may be largely an electron recombination with ions and not one of ions with ions. The value of U or K for the positive ion would not then enter in, and only the value of U for the electron would count. In pure N_2 or H_2 this chance is relatively great, as the electrons remain free for as long as $1/10$ sec. or more. To study this question theoretically, inquiry may be made as to the length of time taken for an electron to recombine, or, rather, electron recombination should be discussed.

Before taking up this subject perhaps another point must be brought up. This concerns the applicability of the Thomson consideration as well. It was tacitly assumed in the Richardson and Thomson calculations that those ions which did not lose energy in the sphere d separated to infinity and had to begin their reunion over again, or with some other ion. Now, actually, if recombination does not occur, the ions may separate a mean free path or two, where, after collisions with molecules, they must lose the kinetic energies due to their attractions. They will then again drift together, but this time a relatively small distance. Thus the recombination for these ions which do not suffer a molecular impact on first coming together is no longer conditioned by the random distribution of the ions, and should take place more rapidly, that is, the factor ϵ may not be correct in its application and may have to be increased by an amount which determines the greater probability of recombination of those ions which missed a first encounter. Just how this could be done for the factor ϵ is difficult to see. It is perhaps true that the effect of the fields of the ions are limited to such small distances that the action outlined above is negligible. This would be more apt to be the case if the effect of the charges can be neglected as is the case with the Thomson theory. However, as even 10 free paths away the field is 14 volts/cm, the possibility cannot be entirely ruled out. The question becomes more acute for an electron recombination.

In this case the elasticity of electron impact requires that the electron make thousands of impacts in the neighborhood of the ion to lose its kinetic energy. This it may do in the neighborhood of the ion, owing to the intense field of the ion and its small mass curving its path continually, so that it cannot escape very far.

From this point of view the problem had best be considered from the standpoint of two time periods, the first being the one required for the ion or electron to come to within a free path or two of the ion of opposite sign, the other the time for the ion or electron to lose its energy and thus to be captured. Just how this can be done is difficult to say at present. A brief analysis of the question may, however, not be out of place. From the definition of α, one has $\frac{dn}{dt} = -\alpha n^2$. Integration of dn from n_o to $\frac{n_o}{2}$ and for dt from 0 to T_o leads to the expression

$$\alpha = \frac{1}{n_o T_o},$$

that is, α is dimensionally volume divided by time, for $n_o = \frac{a}{V}$, where a is a number, V is a volume, and T is a time. Thus $\alpha = \frac{L^3}{T}$ dimensionally. Regarding both the Langevin and the Thomson equations for α, in both cases ϵ is a pure number. In Thomson's equation then there is left

$$\alpha_T = \pi d^2(U_A{}^2 + U_B{}^2)^{1/2},$$

and from Langevin's equation

$$\alpha_L = 4\pi(K_+ + K_-)e.$$

In the first case d is a length and $\sqrt{U_A{}^2 + U_B{}^2}$ is a velocity. Hence Thomson's α_T is dimensionally correct. Langevin's α_L is a velocity in unit field divided by a field strength, and multiplied by a charge. This dimensionally yields L^3T^{-1}, and hence this equation is also dimensionally correct. In both cases α gives the cm^3 per second swept out by the recombination area of the ion. The time element sought would then be the time taken to sweep out a volume which would contain another ion so as to capture it. In Thomson's equation it would be the average length of a cylinder swept out which would contain one ion of the opposite sign. Since the capture is effected in a cylinder of base πd^2, the time characterizing it would be $\frac{l}{(U_A{}^2 + U^2{}_B)^{1/2}}$ when $\pi d^2 l = \frac{V}{a}$, V being the volume in which a ions of opposite sign

occur. Accordingly, the time t_d characterizing recombination will vary with the ion density. In Langevin's theory, it would be the time defined by $t_d = \dfrac{\sqrt[3]{\dfrac{V}{a}} - d}{\bar{v}}$, $\bar{v} = \dfrac{\displaystyle\int_{\sqrt[3]{\frac{V}{a}}}^{d} 4\pi(K_+ + K_-)\frac{e}{r^2}dr}{\displaystyle\int_{\sqrt[3]{\frac{V}{a}}}^{d} dr}$,

and so it also would depend on the ion density. Experiment has shown that α was too large, and hence the times characteristic of this phase of recombination, are too small, that is, α was multiplied by a factor ϵ, or t_d must be multiplied by $\frac{1}{\epsilon}$ to give the correct value for these quantities. The ϵ was computed on the assumption that two ions that did not recombine returned to their *status quo.* This, it was stated, might be incorrect. In the sense of this discussion $\frac{1}{\epsilon}$ must be replaced by an expression in terms of the time factors. It might be represented by $\frac{t_d + t_r}{t_d} = \frac{1}{\epsilon}$. Here t_r is the time of recombination when they get within d of each other and t_d is time to reach a distance d. Now while t_d must be estimated as a function of ion density, it can be discussed for a given $\frac{a^*}{V}$. It may or may not be a function of pressure. In the Thomson theory it is not, while in the Langevin theory it is. On the other hand, t_r is a function of the gas pressure. It is difficult to estimate t_r alone for gas molecules. It would depend on the number of times that it left the proximity d of the ion and the distances which it covered before it lost its energy. The values of ϵ observed give the relative values of t_r and t_d at different pressures, if constant ion density is assumed. At high pressures in air, $\epsilon = 0.9$, thus $t_d = 9t_r$. At about 100 mm, ϵ may become 0.2 and $8t_d = 2t_r$. This may indicate that at low pressures the ion goes so far from the companion ion that the time taken to lose its energy is four times the initial time of approach.* It is quite probable

*As t_d varies with the concentration increasing as time increases it is seen that unless t_r increases in the same ratio with concentration, values of α for low concentrations will depend entirely on t_d. How t_r varies with concentration one cannot say. If it varies little then ϵ and hence the α deduced from experiment will be a function of concentration and of time.

that here the assumptions of the Richardson-Thomson calculation of α are fulfilled. Thus the analysis in this case has proved of little avail. There is, however, a case where t_r has such a value that it must be considered in connection with t_d. In order to decide whether the electron plays a rôle in ion recombination or not, α must be calculated for the electron. In this case, t_d can be easily computed for a given $\frac{a}{V}$, but it is much less than t_d for ions, while t_r may not be so. Before calculating t_r for electrons, t_d could be calculated for ions and electrons, taking 10^6 ions per cm,^{3} a possible number in experimental work. Taking this and calling $\epsilon = 1$, t_d from Thomson's equation for N_2 gas is obtained as 0.26 sec. for ions and 0.0016 sec. for electrons. From the Langevin theory, t_d for ions is 0.18 sec. and t_d for electrons is about 2.0×10^{-6}, using the value for electron mobilities found in N_2 by Loeb. In gases like N_2 and H_2 the electrons can remain permanently free. In O_2 they attach to form ions, on the average, after some hundred thousand impacts with molecules. The question then arises whether it is possible that electrons combining with molecules can materially influence α. To see this, t_r for electrons must be computed. J. J. Thomson has computed α for electrons in the article cited above. His calculation is in error, as he replaces the electron mean free path in the ion equation for low pressures by what he terms an energy free path for the electron. This is not legitimate, as the mean-free-path factor $\frac{1}{\lambda}$ of the equation is deduced on the probability of *one* impact inside of d and assumes a straight path. The energy free path is in no sense straight, and it is doubtful if the concepts can be interchanged. Also he uses a very high value for energy loss on impact that is not warranted by experiment. The analysis may then be resorted to, considering the times t_d and t_r, to test α for electrons. The values for t_d have already been computed for electrons and set at 1.6×10^{-4} or 2×10^{-6} sec., depending on the equation used for the computation. According to quantum theory, it is probable that the electron in impacts with gas molecules such as N_2 loses only a small fraction of its energy at each impact. This fraction may be as low as 0.000038 of its energy for N_2. The time t_r may be computed from the time rate of energy loss or impact. If P is the number of impacts of electrons with molecules per unit time, f the fractional loss of

energy at an impact, then $\frac{dE}{dt}$, the rate of loss of energy, is given by $\frac{dE}{dt} = Pf\,E$, where E is the energy. Now for an electron P is a function of E, for the greater the energy the faster the electron moves. If P_o be the number of impacts per second at N.T.P. and E_o be the energy of the electron under those conditions,

$$P = P_o\sqrt{\frac{E}{E_o}}.$$

Whence,
$$\frac{dE}{dt} = -\frac{P_o}{\sqrt{E_o}}\sqrt{E^3}.$$

Integrating E from E to E_o, and t from 0 to t,

$$\frac{+\sqrt{E} - \sqrt{E_o}}{\sqrt{E}} = \frac{1}{2}P_oft.$$

Now λ for an electron is $4\sqrt{2}\lambda$ for N_2 molecules, or 5.34×10^{-5} cm, and U_A for the electron is about 1.15×10^7 cm/sec. Whence P_o is 2.15×10^{11}, $f = 3.8 \times 10^{-5}$, and $E_o = 5.6 \times 10^{-14}$ ergs. The radius of the orbit of the electron about the ion might be set as 4×10^{-8} cm when captured. Then E, the energy to be dissipated, would be $\frac{1}{2}\frac{e^2}{r}$ if the orbit is circular, that is, $E = 2.85 \times 10^{-12}$ ergs. From this t_r may be calculated as $t_r = \frac{2(\sqrt{E} - \sqrt{E_o})}{P_of\sqrt{E}} = 2.1 \times 10^{-7}$ sec. In any case t_r is less than t_d from these calculations. It is, however, doubtful whether the electron recombination may be calculated in this fashion at all. It may be governed by quantum conditions and the probabilities of capture of the electron and of radiation may be the determining factor. Thus t_r may be a much longer process than here computed. It seems, however, on the whole, reasonable to assume that the electrons recombine with positive ions faster than negative ions do. It is even probable that α for electrons is some 60 times as great as α for ions. In this case it is extremely probable that the initial recombination rate of carriers in gases should give a different value of α than the later periods in gases where the electrons have attached to form ions. But all accurate experimental data are lacking. What is required at present is more careful measurement of α by a direct method, over large ranges of time and pressure, in carefully purified gases

of two classes, those in which electrons do not attach and those in which they attach. Until this is done, further theoretical discussion is useless.

111. The Mobilities of Electrons.—According to the elastic collision theory of Langevin for the mobility of a charged carrier, derived in Sec. 105, the mobility of such a carrier is given by

$$K_e = 0.815 \frac{e}{m} \frac{\lambda_1}{C_1} \sqrt{\frac{M + m}{M}},$$

where m is the mass of the carrier, C_1 the square root of its mean squared velocity, M the mass of the gas molecule, λ_1 the free path of the carrier, and e its charge. This equation should be theoretically applicable to the case of the electron where m is the mass of the electron, C_1 the square root of its mean squared velocity of agitation, and λ_1 its free path. For ordinary cases, λ_1 is $4\sqrt{2}$ times the mean free path for the uncharged gas molecules (see Sec. 24). Under certain conditions, electrons in gases have abnormally long mean free paths (see Sec. 25), and where such occur the equation must be modified to include this fact. The mean free path of the electron, due to its much higher velocity, does, however, not appear to be reduced by the presence of its charge, in the same way in which this holds for the ions. At any rate, it may, for the general case, be assumed that the value of λ_1 for an electron is $4\sqrt{2}$ that of the molecules. It might then be expected that the mobility of the electron could be computed by assuming C_1 a constant given by the velocity of thermal agitation of the gas. Now this is not the case. Franck and Hertz[52] were among the first to show that the electron in monatomic gases makes almost completely elastic impacts with the atoms. The many investigations on resonance and ionization potentials have shown that this is largely true, for all gases, unless the electron has an energy $\frac{1}{2}mC^2$, which is great enough to excite one of the electrons of the atom or molecule to emit light, or to remove that electron, that is, there seems to be no or little loss of energy on impact between electrons or molecules unless the electron has an energy $\frac{1}{2}mC^2 = h\nu$, where ν is the frequency of the light emitted and h is the Planck constant. For most gases $h\nu$ leads to an energy equivalent to a fall of potential of several volts, that is, to an energy of 10^{-12} ergs. The reason for this is quite clear. Unless on an impact the energy of the electron goes to deform the atom or molecule,

that is, to displace one of its electrons, its energy loss must obey the laws of elastic impact. The quantum theory says that the deformation cannot take place unless the electron has the quantum of energy to move one of the molecular electrons to one of the outer orbits. This it cannot do except under the conditions above. Now in an elastic impact the electron transfers an energy to the molecules which depends on the relative masses. It is given by the relation

$$f = 2\left(\frac{m}{M}\right)\left(1 - \frac{M\omega^2}{mC_1^2}\right),$$

where $\frac{M\omega^2}{2}$ and $\frac{mC_1^2}{2}$ are the average kinetic energies of molecules and electrons, m is the mass of the electron, M that of the molecule, and f the fraction of the energy lost at an impact. For the case where $C_1 >> \omega$, $f = 2\frac{m}{M}$. For a N_2 molecule and an electron, $f = 0.0000384$, and for the helium atom, it is 0.00027. Thus the loss of the energy is very small. An analogous mechanical example would be the loss of energy of a perfectly elastic tennis ball thrown against the side of a small boat, where, owing to the great mass of the boat, the loss of energy of the tennis ball to setting the boat in motion would be very small indeed. The very small energy transfer to a molecule by an electron explains why the electron only loses larger amounts of energy to electrons.

The value of ν_2, the frequencies of rotations of the molecules, and ν_1, the frequencies of atomic vibration, are much lower than the values of ν_2 for electrons. Thus the rotation quanta $h\nu_2$ and the vibration quanta $h\nu_1$ are much smaller than the value of $h\nu$ for the emission of visible light. Since, however, the electron is not able to impart energy to the massive atoms of the molecules, because of its small mass, the losses of the electron energy to these sources are also negligible,* so that, apparently, electrons below 2 volts' energy in such gases should rebound elastically with energy losses of the order of $f = 2\frac{m}{M}$ only. This is held by some to be the case. It is observedly true for the case of electrons and He atoms, according to Compton's[53] measurements.

* It appears, however, that in some molecules the initial levels of the electrons in the normal molecules have several equilibrium positions separated by small amounts of energy. If transitions can be caused between these in the unexcited state, then smaller energy losses are possible.

It is possible that the impacting electron might strike one of the valence electrons holding the molecules together. This could cause a disturbance in the binding forces of the atoms in the molecule, and if the energy loss were greater than $h\nu_1$, vibration would result. The probability of this is, however, very small. In other gases, greater losses appear to have been observed of as much as several per cent. If these are correct, the loss seems in contradiction to the general experience of the application of the dynamical equations to this type of electron impact. There seems to be a legitimate doubt about the correctness of the conclusions from the experiments, owing to their complexity and the presence of disturbing factors, so that at present the question is an open one. For the sake of simplicity, one can assume that up to real resonance potentials in all gases f is given by the above expression.

With the low rate of energy loss, one can turn to the behavior of an electron in a gas where an electrical field of low value exists. Here between impacts the electron gains an energy Xed from the field X, where e is the electron and d the component of the electron free path in the direction of the field. This energy plus the energy of thermal agitation it retains at its impact, except for the fraction f, which it loses. As f is small, the energy will be practically that gained in the field. As this goes on over several free paths, the energy of the electron mounts higher and higher. The energy gained, however, results in an increased velocity, which, owing to the electron's small mass, is not directed along the field, but takes on all directions which the random motions of the electron, as a result of the collisions, demand. Thus what really happens is that the electron gains in energy and velocity, but the velocity is not in the direction of the field but a randomly directed velocity, or a heat motion. The temperature of the electron in virtue of the external field increases above that of the surrounding gas molecules. This process will go on until the fractional energy loss multiplied by the average energy of the electron equals the average rate of gain of energy by the electron from the field. The electron then reaches a steady state when it loses energy at impacts as fast as it gains it from the field. It has then gained its *terminal* velocity in the field, and it has a terminal energy well above that of the gas molecules about it. If the field is cut off it loses this gradually, eventually attaining equipartition. If the field is high, the electron may gain resonance energy before

it reaches the terminal state. It will then collide inelastically and again start from rest. In the mobility measurements the fields are such that this never occurs, so that it will be overlooked.

Accordingly, in the mobility measurements where the electron gains its terminal speed very soon, the factor mC_1^2 is not the energy of agitation of the molecules of the gas, but a much larger quantity. To Townsend[15] belongs the credit of having seen this first. He represents the value of C_1 as $\sqrt{k}C = C_2$, where k is the ratio of the energy of the electron in the field to the energy of the agitation of the molecules. This k he succeeded in evaluating from measurements which he made of the diffusion of electrons at low pressures. Thus he found for electrons in air the values given in the table below:

p in mm	X in volts/cm	$\frac{X}{p}$	k
18.5	40	2.16	24.0
12.0	30.	2.5	26.0
1.8	4	2.2	24.0
3.7	40	10.8	46.0
1.8	20	11.1	46.5
0.95	10	10.5	45.5

These show that k is considerable and that it depends on the ratio of field strength X to pressure p. In the latter case the value by which C would have to be multiplied to give the true value would be about 6.8. It is obvious that the terminal energy and hence the factor k must vary with the field strength, the free path, and the value of the quantity f. The first attempt at a theory of this was made by Loeb[2] in 1921. Later Compton[3] took up the computation from the standpoint of his measurements on f and arrived at an interesting theory, which, in the absence of more definite information about some of the quantities entering into the equation (notably λ_1), leads to satisfactory agreement with Townsend's[54] results for electron mobility. In what follows, Compton's treatment of the problem will be given. Compton starts, as was done above, from the Langevin equation for electron mobility

$$K = 0.815\frac{e}{m}\frac{\lambda_1}{C_1}\sqrt{\frac{m+M}{M}} = 0.75\,\frac{e}{m}\frac{\lambda_1}{\bar{c}_1},$$

as m is small compared to M. In a field X the average distance which an electron advances in a second in the direction of the field

is KX. But $\frac{\bar{c}_1}{\lambda_1}$, is the average number of impacts made in 1 sec. Thus S, the average advance of the electron in the field between successive collisions, is

$$S = \frac{KX}{\frac{\bar{c}_1}{\lambda_1}} = 0.75\frac{\lambda_1^2 eX}{m\bar{c}_1^2}.$$

Converting

$$\bar{c}_1 = \sqrt{0.849}C_1$$

and calling $eU = \frac{1}{2}mC_1^2$, then $S = 0.441\frac{\lambda_1^2 X}{U}$.

U is thus the energy of the electron in equivalent potential drop. As was stated before, the fraction of the energy lost at each impact of an electron with a molecule follows from simple dynamics.[3] It is given by

$$f = 2\left(\frac{m}{M} - \frac{\omega^2}{C_1^2}\right) = 2\frac{m}{M}\left(1 - \frac{\Omega}{U}\right),$$

where Ω is ω in equivalent volts. The terminal speed may at once be computed, for in going a distance dx in a field the electron gains an energy $eXdx$, and it loses an average of feU at each of the $\frac{dx}{S}$ intervening collisions. The net gain in energy is

$$edU = eXdx - feU\frac{dx}{S}.$$

Putting in the values of f and S from above,

$$\frac{dU}{dx} = X - 4.536\,mU\frac{(U - \Omega)}{\lambda_1^2 MX}.$$

To get the terminal speed, it need only be remembered that when this is arrived at $\frac{dU}{dx} = 0$. Thus,

$$U_t = \frac{1}{2}\Omega + \sqrt{\frac{\Omega^2}{4} + \frac{\lambda_1^2 MX^2}{4.536m}},$$

in equivalent potential drop. If this be transformed to terms of $\frac{1}{2}mC_2^2 = Ue$, and the mean energy of the molecules is given as $e\Omega = \alpha T = \frac{1}{2}MC^2$, and, if $C_2 = 1.086\bar{c}_2$, then

$$(\bar{c}_2)_t = \frac{1}{1.086\sqrt{m}}\left[\alpha T + \left(\alpha^2 T^2 + \frac{\lambda_1^2 MX^2 e^2}{1.134m}\right)^{\frac{1}{2}}\right]^{\frac{1}{2}}.$$

For many cases $e\Omega$ or αT is so small that it can be neglected, so that

$$(\bar{c}_2)_t = 0.891\left(\frac{\lambda_1{}^2 Xe}{m}\sqrt{\frac{M}{m}}\right)^{\frac{1}{2}}.$$

Accepting $\lambda_1 = 4\sqrt{2}\lambda$, U_t may be computed as a function of $\frac{X}{p}$, the field strength in volts per cm divided by the pressure in mm of Hg. The results of such a computation for several gases are given below:

Gas	$\sqrt{\frac{M}{m}}$	λ_1(in cm)	U_t (volts)
He	85.9	0.1313	$5.30\,\frac{X}{p}$
A	271.5	0.0461	$5.86\,\frac{X}{p}$
H_2	60.8	0.0842	$2.40\,\frac{X}{p}$
N_2	227.4	0.0435	$4.65\,\frac{X}{p}$
CO_2	285.0	0.0290	$3.88\,\frac{X}{p}$
Hg	608.0	0.0135	$3.85\,\frac{X}{p}$

This table holds for $\frac{X}{p}$ of such a value that U_t is considerably greater than a value of $\Omega = 0.0372$ volt, the mean velocity of thermal agitation. It also holds only below values of $\frac{X}{p}$ where U_t is less than a critical potential for resonance. When an electron has the terminal speed under the conditions specified above, the average number of impacts per cm advance in the gas is given as

$$\frac{1}{S} = \frac{1.065}{\lambda_1}\sqrt{\frac{M}{m}}.$$

It is of advantage to know how rapidly the electrons acquire their terminal speeds, that is to say, how far from the cathode they get before they acquire them. This is obtained from the value of

$$\frac{dU}{dx} = X - 4.536mU\frac{(U - \Omega)}{\lambda_1{}^2 MX}.$$

Designating the constant $4.536\,\frac{m}{\lambda_1{}^2 M} = \frac{4.536p^2 m}{\lambda^2{}_{10}M}$ as α, and inte-

grating from $U = 0$ at $x = 0$ to $U = U$ at $x = x$, then U at x cm from the cathode, is

$$U = \frac{1}{2}\Omega + X\sqrt{\frac{1}{\alpha^2} + \frac{\Omega^2}{4X}}\,\frac{e^{2\alpha^2\sqrt{\frac{1}{\alpha^2}+\frac{\Omega^2 x}{4X^2}}} - 1}{e^{2\alpha^2\sqrt{\frac{1}{\alpha^2}+\frac{\Omega^2 x}{4X^2}}} + 1}.$$

If $X = 0$, $U = \Omega$, and if the field is so large that Ω may be neglected

$$U = \frac{X}{\alpha}\,\frac{e^{2\alpha x} - 1}{e^{2\alpha x} + 1}.$$

When x is large U approaches $U_t = \dfrac{X}{\alpha}$.

The distance d that an electron has to go so that its energy is reduced to a fraction ϕ of its terminal energy can be obtained by setting $\dfrac{U}{U_t} = \phi$ and solving for the particular value of $x = d$ required. It comes out that

$$d = \frac{1}{2\alpha}\log\frac{1 + \phi}{1 - \phi}.$$

The average number of collisions μ made in going x while getting their terminal speed is

$$\mu = \int_0^x \frac{1}{S}dx = \int_0^x \frac{U}{0.441\lambda_1{}^2X}dx,$$

for

$$\frac{1}{S} = \frac{U}{0.441\lambda_1{}^2X}.$$

From the equation for U, this is

$$\mu = \left(\frac{M}{4m}\right)[\log\,(2 + e^{2ax} + e^{-2ax}) - \log 4].$$

Thus the average number of collisions μ made in acquiring ϕ is obtained by putting d for x in the above

$$\mu_\phi = \frac{M}{4m}\log\frac{1}{1 - \phi^2}.$$

These results are summed up in the table on page 503. They are of use where the question of the terminal velocities of electrons enters in.

p, in mm	ϕ	He, d in cm	N_2, d in cm	Hg, d in cm
760	0.1	0.00064	0.00057	0.00047
	0.2	0.00131	0.00115	0.00096
	0.5	0.00356	0.00313	0.00262
	0.9	0.00953	0.00840	0.00708
	0.99	0.01710	0.01507	0.01260
10	0.1	0.049	0.043	0.036
	0.9	0.724	0.638	0.533
1	0.1	0.49	0.043	0.360
	0.9	7.24	6.38	5.33

From the value for U_t and thus $\bar{c}_{2t}$, the electron mobility can be at once obtained, for it is merely necessary to replace the C_1^2 of the Langevin equation for electron mobility by this factor to get K_e the electron mobility. Thus K_e becomes

$$K_e = \frac{0.815e\lambda_1}{\sqrt{m}\left[\alpha T + \left(\alpha^2T^2 + \dfrac{\lambda_1^2 MX^2e^2}{1.134m}\right)^{1/2}\right]^{1/2}}.$$

When the terminal velocity is large compared with the molecular velocities, the equation reduces to the form

$$K_{e_1} = 0.842\sqrt{\frac{e\lambda_1}{X\sqrt{Mm}}} = 0.707\sqrt{\frac{e\lambda_1\sqrt{f}}{Xm}}.$$

The complete mobility equation in terms of α is then

$$K_e = \frac{0.815\,e\lambda_1}{\sqrt{m}\left[\alpha T + \left(\alpha^2T^2 + 1.76\lambda_1^2\dfrac{X^2e^2}{f}\right)^{1/2}\right]^{1/2}}.$$

It is seen here that the mobility is not a constant but is a function of $\frac{X}{p}$, for $X^2\lambda_1^2$ is $\left(\frac{1}{p}\right)^2 X^2\lambda^2_{10}$, where λ_{10} is the mean free path at one mm. As $\frac{X}{p}$ increases, it is obvious that K_e will decrease. Thus the velocity of the electron in a gas in an electric field increases more slowly than proportionally to the field strength. It is obvious that the greater the inelasticity of impact (*i.e.*, the greater the fractional loss of energy at an impact f) the less the value of K_e will depart from a true mobility, and the more slowly K_e will vary with $\frac{X}{p}$.

The equation can be compared with experiment by remembering that $\lambda_1 = \frac{\lambda_{10}}{p}$. Doing this the mobility constant (the mobility reduced to 760-mm pressure and 0°C.) K_{e_0} is given by

$$K_{e_0} = \frac{2.54 \times 10^5 \lambda_{10}}{\left[1 + \left(1 + 1.355 \times 10^6 M \lambda^2_{10}\left(\frac{X}{p}\right)^2\right)^{\frac{1}{2}}\right]^{\frac{1}{2}}}$$

It remains, therefore, only to put in the values of M, λ_{10}, and $\left(\frac{X}{p}\right)$ to get K_{e_0}.

The results for H_2 are given in Fig. 72. The crosses represent Townsend and Bailey's[54] data, the points Loeb's data, taken by a

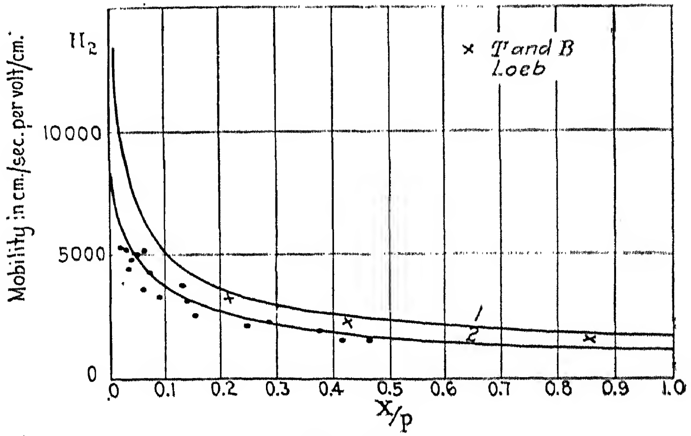

FIG. 72.

more direct but more fallible method. The mobility K_{e_0} is plotted as ordinates in cm/sec. against $\frac{X}{p}$ in volts/cm per mm pressure. The smooth curves 1 and 2 represent the theory for $\lambda_{10} = 4\sqrt{2}\lambda_0$ for H_2 molecules, and $\lambda_{10} = 0.58\ (4\sqrt{2})\lambda_0$ for H_2 molecules. The former curve fits Townsend and Bailey's data better than does the latter.

The results in N_2 are given in Fig. 73. The results of the different workers are represented as before. In this case the one result of Townsend and Bailey in the region studied by Loeb agrees with his values fairly well. The smooth curve 1 is calculated from theory, assuming that the mean free path for N_2 has the value $4\sqrt{2}\lambda_0$ for molecules $= 0.0405$ cm at 1-mm pressure.

This does not fit the data. By choosing $f = 0.05$, instead of 0.000038, the true value, curve 2, is obtained. This fits the data less well than curve 1. Finally, if f is taken as 0.000038 but λ_{10} is taken as $4(4\sqrt{2}\lambda_0)$, or 0.1620 cm at 1-mm pressure, curve 3 is obtained. This conclusion that the mean free path in nitrogen is longer than the kinetic-theory value was drawn by Loeb from his original measurements. The existence of abnormally long mean free paths of electrons in some gases has been shown by Ramsauer, Mayer, and Brode (see Sec. 25). They were not found in N_2 at the higher velocities worked at. It is possible that at the low terminal velocities at $\frac{X}{p} = 0.1$, where U_t is less than

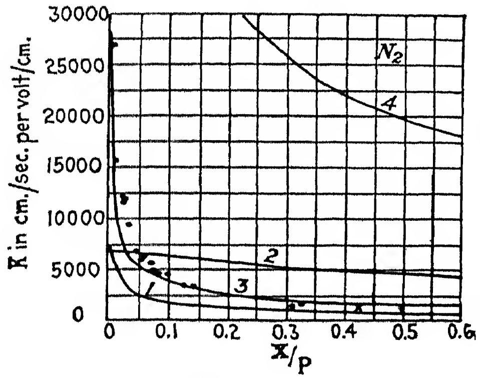

FIG. 73.

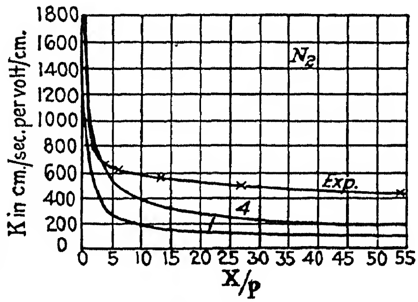

FIG. 74.

0.4 volt, the N_2 which is similar to argon also shows abnormal mean free paths. The points at higher values of $\frac{X}{p}$ and of U_t fall nearer the curve with the normal value of λ_{10}. Another striking confirmation of the theory was made by Wahlin[55] in N_2 at low values of $\frac{X}{p}$, that is, near 0.01, at the same time as Compton's paper was in press. The peculiar intercept of the theoretical curve with the axis of ordinates was experimentally observed in N_2 by Wahlin. The latter, however, treated his curve in a different manner theoretically. He finds that a λ_{10} which varies with velocity is needed. He also employs a higher f to attempt to get agreement. This, in view of the theoretical considerations, is improbable. Curve 4 in Fig. 73 is the case for N_2 when impacts are completely inelastic. It is seen that K is much

higher than the observed values. In Fig. 74 the values of Townsend and Bailey at high values of $\frac{X}{p}$ are given. Up to $\frac{X}{p}$ equal to about 5, the curves fit fairly well. Beyond this the observed values are distinctly higher than the theory demands. Compton concludes that this represents an increase in f due to inelastic impacts, for here U_t is 23 volts in magnitude, which lies well above the ionization potential for N_2.

In Fig. 75 are given the results of Loeb in He. They are more in accord with the theoretical curve 2, for which λ_{10} is 0.5, the kinetic-theory value, than with 1, for which λ_{10} comes from the kinetic theory. The curve for O_2 (Fig. 76), represented by

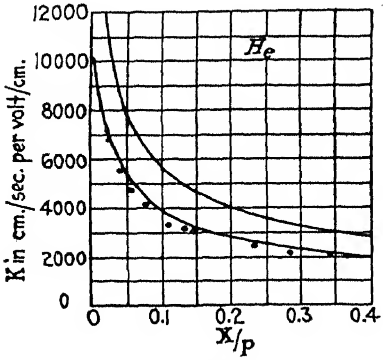

FIG. 75.

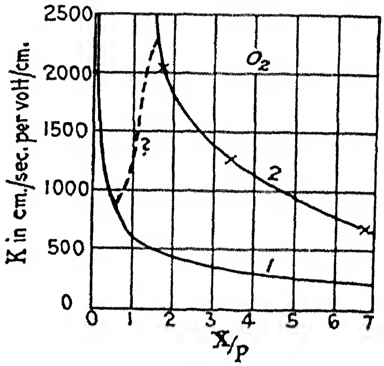

FIG. 76.

crosses, comes from the data of Townsend and Bailey. This is the worst failure of the theory, for using f and λ_{10} from the kinetic theory the computed curve is given by the full curve 1. Measurements in this gas, however, are highly questionable, as the electrons, on the average, in 40,000 impacts attach to form ions. It is, however, quite possible that in this gas the electrons suffer less elastic impacts than in the other gases studied. A higher value of f would explain the result better than a higher λ_{10}. It may be noted that the measurements in O_2 correspond to about 8 volts' terminal velocity where inelastic impacts could be expected to begin.

The conclusion which can be drawn from the applications of the kinetic theory to the problem of electron mobilities is that the theory, in spite of the complexity of the problem, is more than qualitatively successful. It is probable that when the alter-

nating-current method of measuring K_e can be perfected by the use of a high-frequency alternating potential of square wave form the critical results at a low value of $\frac{X}{p}$ will make it possible to get good estimates of f and λ_{10} in the gases considered.

112. Attachment of Electrons to Neutral Molecules in Gases to Form Ions.—It was stated in Sec. 104 that the mobility of negative ions in gases was inversely proportional to the pressure down to very low pressures when ions that had been already formed were measured. Before the work of Wellisch[8,56] in 1915 this was not believed to be the case. It was observed by many workers that the mobilities of photoelectrically generated ions, measured soon after liberation from a metal plate in the measuring field, began to become abnormally great at 100-mm pressure in air. This was ascribed by numerous observers to a breaking up of the negative ion cluster by impacts with gas molecules. To Wellisch is due the credit for having investigated the mobilities of negative ions when formed behind a gauze, at low air pressures, after they had come through the meshes of the gauze. He found two classes of carriers, one which he showed were normal ions of a mobility constant close to the value accepted for normal negative ions, the other which he asserted were free electrons. The effect of the gauze and the weak auxiliary field back of it was to delay the photoelectrically liberated electrons, or electrons which were caused by radium radiations, until they formed ions. This Wellisch did not know. In fact, as he did not compare his results with the results of workers who had used no gauze, he devised another explanation. He assumed that an electron, when liberated, must have the energy ϵ_0 necessary to attach to a molecule to form an ion. If it has not this energy it will never attach and will remain permanently free. Thus one has either ions or permanently free electrons. In 1920, Loeb[9] undertook the problem and repeated Wellisch's experiments. He completely corroborated the observations of Wellisch. But he further observed that the relative number of ions and free electrons depended on the pressure and auxiliary field strength which allowed of only one interpretation. It showed that the free electrons were not permanently free. In fact, it showed that ion formation was contingent on condition that the electrons spend a sufficient time in the auxiliary field before being studied. If the pressure and field strength were such that the time was short, only electrons were obtained; if

the time was long, only ions were obtained. By increasing the auxiliary field strength so that the electrons had a very high energy, no increase in the number of ions formed was observed by Wahlin,[51] who was then working with Loeb. Thus the Wellisch theory was found to be wrong.

The experimental work and viewpoint on this problem were very much aided by a theory of J. J. Thomson.[16] Thomson attempted to explain the abnormal increase of mobility of photo-electrically liberated ions at low pressures in air as follows. The ultra-violet light used liberates electrons. These do not attach to molecules to form negative ions at their first impact. If it be assumed that the electron requires, on the average, n impacts before it can attach to form an ion, where n may be a large number, then it is possible to explain the phenomenon. This amounts to assuming that the attachment of an electron is a chance phenomenon, depending on where it strikes the molecule or under what energy conditions the impact takes place. For each chemically different gas this would be different, depending on its chemical nature. For simplicity, Thomson assumed n to be a constant, independent of velocity, characteristic of each gas. That this is probably incorrect in some measure will be seen later. As a first approximation, it is, however, sufficient.

This constant n has other interests. Many discharge-tube phenomena had indicated that in certain gases the electrons apparently did not remain free, or were not present. In others they appeared to be so. It was Franck[57] in 1910 who first found that in carefully purified He the negative carriers had a mobility of several hundred cm/sec., while the positive carriers had the mobility of the normal ions to be expected in He. He interpreted these results as meaning that the negative carriers in He were free electrons. He found the same to be true in Ar and N_2 gases. In the latter gas he gave the value of 200 cm/sec. observed for the negative carriers, as the electron mobility in N_2 at atmospheric pressure. It was the observation by Loeb of mobilities of over 1000 cm/sec. in N_2 on repeating Franck's work which led to the electron-mobility investigations discussed in Sec. 111. Franck concluded from his investigations that the gases had electron affinities which varied with the chemical nature of the gas. This term was also associated with the electrical charge taken in polar compounds by the atoms. Thus, atoms like H, Na, Mg, or Al were called *electropositive,* while O

and Cl were electronegative. That He and Ar, which are inert gases, should leave the electrons free was not surprising. N in many cases, however, is chemically electronegative, while the N_2 molecule seemed to shun electrons as much as He. The more electronegative gases like O_2 and Cl_2 were, owing to their association with the electronegative atoms, considered to be admirable electron traps. This was borne out by their behavior in discharge tubes. It is, however, known today that the electropositive or electronegative character of an elementary atom is a property of the atom, due to the fact that the stable outer configuration of electrons in the atom seems to build around the number 8 in certain portions of the periodic table.[58] This striving towards completion of an octet, however, is definitely applicable to the atomic state. It depends on the nature of the electronic configuration of the molecule* whether the addition of an electron to its configuration will increase its symmetry and therefore its stability or not. At the present time this is not predictable for molecules, and the association of electronegativity in the atomic sense with molecules is doubtful.

That electrons do make negative ions in some gases and not in others is, however, an observed fact which need have no relation to the atomic behavior above. The term "electron affinity" may then be applied to describe the behavior of a molecule towards the electron. It is then necessary to find more than a qualitative measure of this property. Two roads to this are open. The one would be to find out what the ionizing potential of the extra electron of the negative ion is. This, of course, could be determined by the frequency of the shortest wave length of the light emitted when an electron is attached to a molecule to form an ion. This multiplied by the Planck constant would give the energy necessary to remove the electron. Up to the present, investigations of this nature have yielded no result and one cannot measure electron affinity in this manner. The second procedure would be to get a quantitative measurement of the average number of the impacts required by an electron with a given type of molecule before it could attach. This quantity

* Recent work in band spectra by Birge and Mullikan indicates close parallelism between molecular spectra and certain atomic spectra. If this is correct the electron affinity of certain molecules can be predicted by a comparison with the atomic species showing similar spectroscopic behaviour.

is precisely the quantity defined by J. J. Thomson as n, his constant of attachment. It is thus necessary to devise a means of determining this. If the number of impacts which an electron makes in going a given distance in a gas under an electrical field could be measured, and if the number of electrons, n_x out of N_0, that transverse a distance x in the gas in the field without attaching could be measured, there would be a means of getting n, the constant of attachment. The number of electrons which go a distance x in a field without attaching must be derived from the assumptions as to n as related to the kinetic-theory constants before the value of n can be computed from any data. To deduce this expression, one may proceed as follows. Assume that it takes n impacts, on the average, for an electron to attach to a molecule, where n is a constant of the molecular type alone. If the average velocity of agitation of the electron is $\bar{c}_2$ and its mean free path λ_1, it makes $\dfrac{\bar{c}_2}{\lambda_1}$ impacts per second. If it is in a field of X volts per cm it moves K_eX cm per second in the field, where K_e is the electron mobility. It therefore takes $\dfrac{1}{K_eX}$ sec. to move a cm in the direction of the field, if it has its terminal speed (see Sec. 111). In this time it makes $\dfrac{\bar{c}_2}{\lambda_1 K_e X}$ impacts. Thus in going x cm in the direction of the field it has $\dfrac{x\bar{c}_2}{\lambda_1 K_e X}$ impacts. If attachment is purely a chance phenomenon, taking, on the average, n impacts for an attachment, the number dy out y electrons attaching between x and $x + dx$ can be written as

$$dy = -\alpha y \frac{\bar{c}_2 dx}{\lambda_1 K_e X},$$

where the quantity $\dfrac{\bar{c}_2}{\lambda_1 K_e X}$ is the quantity by which the distance dx in the field must be multiplied in order to give the number of impacts in going dx cm. In this equation α is a constant to be evaluated from the equation obtained. Thus

$$\frac{dy}{y} = -\frac{\bar{c}_2\alpha}{\lambda_1 K_e X}\,dx,$$

or

$$y = Ae^{-\frac{\alpha\bar{c}_2}{\lambda_1 K_e X}x}.$$

If $x = 0$, $y = N_o$, the number of electrons starting and thus

$$y = N_o e^{-\frac{\alpha \bar{c}_2}{\lambda_1 K_e X} x},$$

that is, y, the number of electrons going x cm in the gas without attaching, is found by multiplying the number N_o starting at $y = 0$ by $e^{-\frac{\alpha \bar{c}_2}{\lambda_1 K_e X} x}$. To get $\bar{x}$ the average distance the electrons go without attaching, one can write

$$\bar{x} = \frac{\int_0^{N_o} x dy}{\int_0^{N_o} dy},$$

and

$$dy = -N_o \frac{\lambda_1 K_e X}{\alpha \bar{c}_2} e^{-\frac{\alpha \bar{c}_2}{\lambda_1 K_e X} x} dx.$$

Call

$$\frac{\bar{c}_2}{\lambda_1 K_e X} = \eta$$

$$\bar{x} = \frac{\int_0^{\infty} -\frac{N_o}{\alpha\eta} x e^{-\alpha\eta x} dx}{\int_0^{\infty} -\frac{N_o}{\alpha\eta} e^{-\alpha\eta x} dx} = \frac{1}{\alpha\eta}.$$

But in going $\bar{x}$ cm the electron has $\bar{x}\,\eta$ impacts. Thus the average number of impacts which the electron makes before attaching is $\bar{x}\eta = \frac{\eta}{\alpha\eta} = \frac{1}{\alpha}$. Therefore $\frac{1}{\alpha}$ is the average number of impacts which the electron makes before it attaches. This is n, the average number of impacts required to attach. Thus the number of electrons out of N_o which go x cm without attaching in a gas is given by

$$y = N_o e^{-\frac{\eta}{n} x} = N_o e^{-\frac{\bar{c}_2}{n \lambda_1 K_e X} x}.$$

It is often more convenient to use this in another form as λ_1 and $\bar{c}_2$ are not known. The equation for electron mobility says that

$$K_e = 0.815 \frac{e}{m} \frac{\lambda_1}{C_2} = 0.75 \frac{e}{m} \frac{\lambda_1}{\bar{c}_2},$$

where λ_1 is the electronic path and $\bar{c}_2$ is the average velocity of agitation of the electron in the field. Thus

$$\frac{\lambda_1}{\bar{c}_2} = \frac{m K_e}{0.75 e}$$

and one has

$$y = N_o e^{-\frac{0.75 e x}{m n (K_e)^2 X}}.$$

As $\dfrac{0.75e}{m}$ is 4.06×10^{17} in electrostatic units, and if K_e is to be given in cm/sec. per volt/cm to correspond with X, this must be multiplied by 300; the equation reads

$$y = N_o e^{-\frac{1.35 \times 10^{15} x}{n (K_e)^2 X}}.$$

The equation holds wherever K_e is known and n is constant. It must be pointed out that the value of K_e is usually measured or computed for electrons where $\bar{c}_2$ has reached a terminal value. In experimental attachment work where n is small this is not the case, and K_e must either be measured directly or else computed for velocities $\bar{c}_2$ that are not terminal velocities.

The first attempts made to measure n were due to Loeb,[17] and later to Loeb[59] and Wahlin.[51] The effect of the attachment and its consequent change of mobility of the carrier on the shape of the current-voltage curves obtained with a square wave form alternating current has been rigorously worked out by Mooney and Loeb. It is given, together with the attempt at experimental verification, in an article by Loeb.[59] The paper shows that it is possible to get a fairly accurate quantitative agreement using the uncorrected electron mobilities taken in air. With the introduction of the corrections to the electron mobilities, agreement is no longer possible. It is probable that, while the electron mobilities as corrected are theoretically more correct, they are really not so correct as the uncorrected ones. The corrected mobilities are lowered in correction and the correction acts to increase the apparent value of C_2 entering into the mobility equation $K_e = 0.815 \dfrac{e}{m} \dfrac{\lambda_1}{C_2}$. Now in attachment not the K_e measured with electrons having a terminal velocity C_2 should be chosen, but a K_e should be used which corresponds to the earlier stages of the electron's career, that is, a higher value of K_e should have been used. This might correspond to the uncorrected value for the mobilities used. The value of n deduced for air from these measurements was about 2×10^5. As electrons do not attach to N_2, these must all attach to O_2 molecules, and n for O_2 should be about 4×10^5.

At an earlier date before the values for electron mobilities were known at higher pressures, Loeb,[17] and Wahlin[51] had measured n for a large number of gases. Using doubtful values of K_e, they arrived at the table of values for n given below. It is questionable whether the values are accurate in more than order of magni-

tude. They do differ, however, so widely in order of magnitude that even these crude early results give a good idea of n. In any case, they are the only estimates to date of this constant in different gases. Further measurements are in progress in several laboratories, using the later knowledge, and it is to be hoped that soon a superior set of values will be available.

ATTACHMENT CONSTANT n

Gas	n	Comment
N_2	∞	
H_2	∞	
CO	1.6×10^8	
NH_3	9.9×10^7	
C_2H_4	4.7×10^7	
C_2H_2	7.8×10^6	
C_2H_6	2.5×10^6	
CO_2	1.5×10^7	Freshly prepared
CO_2	3.5×10^6	4 hours old
CO_2	2.1×10^5	22 hours old
N_2O	6.1×10^5	
C_2H_5Cl	3.7×10^5	
Air	4.3×10^4*	
O_2	8.7×10^3	
Cl_2	Less than 2.1×10^3	

* The value of n for air was later redetermined using more accurate values for K_e. It is about 2×10^5. The value for O_2 was found to be one-fifth of this, in accord with the supposition that the electrons attached to the O_2 in air. The value 2×10^5 is in agreement in order of magnitude with recent more reliable values of Bailey.

While these results are not of more than qualitative value, they are significant, inasmuch as they give a definite though rough order of magnitude of the electron affinity of some gas molecules.

The difficulties in obtaining proper experimental values of n lie in the evaluation of K_e, which must be determined at the same time that n is measured. A further complication is introduced if n depends on $\bar{c}_2$. This is assumed to be the case by Bailey. Bailey[18] tries to overcome the difficulty in measuring K_e by obtaining measurements which determine the quantity $\dfrac{\bar{c}_2}{n\lambda_1 K_e} = \beta$ as a function of $\dfrac{X}{p}$. He does this by measuring the ratios of

the currents passing through holes in a series of plates separated by known distances. The ratios of these currents can, by theory, be related to β, since the relative velocities of diffusion of electrons to the plates is greater than that for ions and can theoretically be computed. The measured ratios then give a factor β which measures the number of attachments per unit $\frac{X}{p}$ per cm distance in the gas as a function of $\frac{X}{p}$. If β is known for a given $\frac{X}{p}$, then by using the relation $\frac{\bar{c}_2}{\lambda_1} = 0.75 \frac{e}{m} \frac{1}{K_e}$ one can get $0.75 \frac{e}{m} \frac{1}{(K_e)^2} \frac{1}{n} = \beta$, and hence $n = \frac{0.75\, e}{m} \frac{1}{\beta} \frac{1}{(K_e)^2}$. From the value of K_e or, better, $K_e X = W$, the velocity of the electron for the same value of $\frac{X}{p}$ taken from the measurements of Townsend and Tizard n can be evaluated. In this fashion Bailey gets $\frac{1}{n}$ for air for certain values of $\frac{X}{p}$ as

$\frac{X}{p}$	0.5	1.0	2.0
$\frac{1}{n}$	3.3×10^{-6}	2×10^{-6}	0.7×10^{-6}
C_2	3.3×10^{7}	4.5×10^{7}	6×10^{7}

The corresponding values of C_2, $(0.92C_2 = \bar{c}_2)$ for $\frac{X}{p}$ are given below the values of $\frac{1}{n}$ as taken from Townsend and Tizard's results. They show that n has the values of 3×10^5, 5×10^5, and 1.4×10^6 in air at increasing values of C_2 of 3.3×10^7, 4.5×10^7, and 6×10^7 cm/sec. His results show that n increases as the velocity of thermal agitation increases. This means that n is not a constant of the chemical nature of the gas alone, but depends on the average energy of agitation of the electron. That n should increase as the energy increases is not surprising, for it is to be expected that, as the electron travels faster, a capture is more difficult to effect. This is in line with Wahlin's results, who found that as the field increased the number of free electrons is not decreased as Wellisch's theory leads one to

expect. The problem, however, requires a further study* by a more direct method for getting β, for the complexity of Bailey's method of finding β is such as to preclude accurate results. This problem is under investigation in the Physical Laboratory of the University of California.

Thus in the domain of electron attachment to form ions one sees how again the kinetic-theory analysis aids in getting quantitative explanations of the processes at work.

113. The Theory of Ionization by Impact by Electrons.—It was shown in the introduction to this chapter that if the photoelectric current in a given field at a pressure p be plotted against the field strength, the current at first reached a saturation value. At higher fields it increased exponentially. This increase was ascribed to the formation of new positive ions and electrons by the electrons initially generated. To Townsend,[19] as was stated, belongs the credit for having worked out the theory of the increase. His experiments showed that, for an initial saturation current i_0 at the surface of the plate $x = 0$, the current i at any distance x from the plate was given by $i = i_0 e^{\alpha x}$, where α is the number of ions generated per cm path by the electrons. This α was then shown by Townsend to be a function of the intensity of the field strength, the pressure p, and the energy required to produce an ion. This relation between $\frac{\alpha}{p}$ and $\frac{X}{p}$ may be deduced as follows, according to Townsend. It can be assumed that the electron makes *inelastic* impacts with the molecules of the gas.†

Thus at each impact the electron starts its free path anew, gaining the energy from the field that it can gain on a free path. As the fields are high, it can be shown that the free paths of the electrons will be so curved in the field that their length will be mainly in the direction of the field. In order to ionize, it was assumed that the electron must strike the molecule with an energy E_0 gained from the field, that is, the energy gained by

* Another aspect of this may be seen in a recent paper by Mohler.[66]

† This assumption was originally made when it was believed that the negative ions, not the electrons, generated new ions by impact. It must now be abandoned, as will later be shown. In spite of the electronic nature of the carriers Townsend maintained that the velocity of the electron at impact with a molecule was reduced to the velocity of thermal agitation so that his theory remains unchanged. (See TOWNSEND, "Electricity in Gases," p. 291, Oxford University Press, Oxford, 1915.)

an electron that ionizes a molecule must be gained in the free fall of the electron through a distance λ_1 in the direction of the field given by $E_0 = Xe\lambda_1$ where λ_1 is the mean free path, X the field strength, and e the electron. Thus the number of ions per cm path generated by an electron must depend on the number of times, in going 1 cm in the gas in the direction of the field, that its free path equals or exceeds a distance x_e given by $x_e = \dfrac{E_0}{Xe}$. Now out of n_0 free paths the number of free paths exceeding a distance x is given by the kinetic theory as $n_0 e^{-\frac{x}{\lambda_1}}$, where λ_1 is the mean free path. Thus if in going 1 cm in the direction of the field the electron makes n_0 impacts with molecules then $\alpha = n_0 e^{-\frac{E_0}{Xe\lambda_1}}$. The number of impacts per cm path n_0 is simply $\dfrac{1}{\lambda_1}$ if, as assumed, the paths are in the direction of the field. Thus

$$\alpha = \frac{1}{\lambda_1} e^{-\frac{E_0}{Xe\lambda_1}}.$$

As $\lambda_1 = \lambda_0 \dfrac{760}{p}$, where p is in mm, one could write

$$\frac{\alpha}{p} = \frac{1}{760\,\lambda_0} e^{-\frac{E_0}{760 e \frac{X}{p} \lambda_0}}.$$

Thus, $\dfrac{\alpha}{p}$ is a $f\left(\dfrac{X}{p}\right)$. For H_2 and one or two other gases Townsend measured $\dfrac{\alpha}{p}$ and, knowing λ, he was able to compute E_0 and test the theory. The agreement observed was quite satisfactory and the value of E_0 deduced for several gases lay in the neighborhood of a free fall of an electron through a potential of 26 volts, that is, $\dfrac{E_0}{e} = V_0$ volts, where V_0 was about 26 or more volts. This measurement of the ionizing potential V_0 was the first estimate directly made.

The situation produced by the satisfactory agreement of the curves with the theory, however, leads to an interesting paradox, for, in the first place, the assumption on which this theory is based, to wit, that of inelastic electron impacts, is wrong. Also,

the exact measurements of the ionization potentials at low pressures by such workers as Franck and Hertz and the countless other investigators in recent years[1c,60] show the values of V_0 computed by Townsend to be in the neighborhood of 50 or 100 per cent too high. It might be added in passing that the essential difference in Franck and Hertz's[52] and Townsend's experiments lies in the fact that Townsend used far greater pressures. Thus his smooth curves are statistical over many free paths, while the low-pressure curves of Franck and Hertz show abrupt changes due to encounters over a single free path. In fact, as will be seen, the theory is far more complicated than it appeared to Townsend in the early days when his theory evolved. That the equation holds as well as it does merely shows that $\frac{\alpha}{p}$ is a function represented sensibly by $e^{-\frac{\gamma p}{X}}$, in which the value of γ was deduced from experiment by Townsend and interpreted in the light of his theory as giving values of V_0 of the order of magnitude obtained, that is, Townsend had an exponential form of equation that fairly well suited the facts, and he suited his adjustable constant V_0 to fit the equation by comparison with experiment.

In 1916, Compton[61] introduced into the problem the new fact, discovered first by Franck and Hertz[52] in 1913 and later carefully investigated for He by himself, that the electrons lost only a very small fraction of their energy on impact with neutral molecules. The considerations of the quantum theory show that there is no loss of energy in impact between electron and molecule unless the electron has the resonance or ionization energy except the fractional loss $f = \frac{2m}{M}$ (where M is the mass of the molecule and m that of the electron), which is demanded by simple dynamics. If this is the case, then, as shown in Townsend's treatment of electron mobilities, the electron gains energy over several free paths, that is, its temperature goes up continually. Thus all electrons would gain the ionizing energy eventually. To carry the idea further quantitatively, Compton had to introduce another notion which was correct in theory. This is that the electron, while it could gain energy over several free paths, did not necessarily ionize on its first impact, but required perhaps many before it could ionize. As the probability of ionization by an electron with the energy E_0 or greater was not

then known, Compton arbitrarily assumed that the probability of ionization P_i had the form

$$P_i = \frac{V - V_0}{V},$$

where V was the volt equivalent of the energy of the electron and V_0 its minimum ionizing potential. The theory which he deduced on the basis of these assumptions fitted the data for He with remarkable accuracy. In fact, it gave a better quantitative agreement than the theory of Townsend. Compton, however, did not have the true form for the function P_i as the later results of Hughes and Klein[62] and Compton and Van Voorhis[63] have shown.* The curve of P_i against V does rise from 0 at V_0 to higher values at values of V considerably above V_0, but it later falls to lower values as V increases. Also, Compton neglected another effect. This is that, while the electron may gain the ionizing energy over very many free paths, it reaches an energy corresponding to the resonance energy long before it gets to V_0 for ionization, that is, if an electron gets an energy corresponding to 4.9 volts in mercury, it will suffer an inelastic impact sooner or later which does not cause ionization, but merely causes the mercury atom to emit light of wave length 2537Å. To ionize the mercury atom, the electron must have an equivalent energy of at least 10.6 volts. Thus if the electrons gain energy slowly, and if they make, on the average, 100 impacts in the region between 4.9 and 10.6 volts required to ionize, an appreciable fraction of these electrons may lose their energy to inelastic impacts of resonance. They will then have to start from rest again to ionize, that is, Compton failed to take account of the possibility of inelastic resonance impacts between resonance and ionizing voltages in his theory. The probability of a resonance impact with the requisite energy is not vanishingly small as shown by Sponer,[65] so that this must be taken into account. With He gas this chance is less than for any other gas, as its resonance potential is about 19.5 volts while its ionization potential is 24.5 volts. If the probability of resonance impacts in such a region were high, say, 0.5, Compton's theory would be

* Recently, Lawrence,[64] has made carefully controlled measurements of the probabilities of ionization and of ionization potentials with electrons of an accurately known speed. He finds that P_i is highest right at the ionizing potential, falling off rapidly after that value. This, when carried over to other gases, will have a material influence on the theory above.

untenable. The theory would then approach one of the original Townsend type. In this case, however, α would depend on the chance that an electron got the ionizing energy in a series of impacts so arranged that it had very few impacts in the resonance region. The first term of the series of exponential terms deduced on such a theory would be the one deduced originally by Townsend.

It is obvious, however, from the small values of P_i and P_r, the ionization and resonance probabilities at the ionization potential (even though these may be the maximum values), that at fields where ionization by collision sets in the *factor which determines α is not so much the chance of getting the ionizing energy on one or more free paths but the chance of ionizing when it has that energy*. The solution of the problem of the value for α, therefore, lies completely in the future and involves the introduction into the equation of the little known probabilities P_i and P_r, as well as the rate of gain of energy from the field. Why it is that the simple relation of Townsend so nearly fits the facts is still a mystery, although an exponential equation with an arbitrary constant in the exponent is quite a flexible equation and can be fitted within the experimental accuracy obtained in such measurements to a rather large group of curves. The deduction of the future correct equation is still as much in the domain of the kinetic theory as the original theory of Townsend. It is only more complicated and perhaps more intriguing because it involves so many more interesting kinetic-theory factors.

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Books Recommended

See Reference. 1, in references to Chap. XI.

APPENDIX I

DIAMETERS OF MOLECULES

The term originates from the original picture of molecules as hard elastic spheres (see Secs. 13 and 14). If two such identical molecular spheres are placed so that they are in contact, the diameter would be defined as the distance between their centers. The contact between the spheres, on such a picture, is defined as the closest approach of the centers on an average impact. The diameter in a solid would be defined as the distance between the centers at equilibrium for molecules arranged in a solid space lattice. This picture, which was adequate until the discovery of the electron, still determines our mode of description in the kinetic theory because of its simplicity.

Actually, molecules are known today to consist of nuclei of positive electricity surrounded by planetary electrons with orbital motions. It is obvious that such configurations of electrical charges cannot be considered hard elastic spheres in the old sense of the term. What really affect the motions of the molecules and atoms are the electrical fields of force between the electrons and nuclei of the atomic configurations. In general, such force fields, with the possible exception of those about the heavier inert gas atoms, are probably force fields with equipotential surfaces which are far from spherical, although perhaps symmetrical about their axes. The force fields are, in general, composed of two sets of forces, forces of attraction of small magnitude varying slowly with the distance (the cohesive forces, or those responsible for Van der Waals' a), and repulsive forces of considerable magnitude which fall off very much more rapidly with the distance (the elastic repulsive forces of the old kinetic-theory molecules). How such opposing forces can occur simultaneously in the atoms is briefly discussed in Sec. 52. The rate at which the force varies with the distance from the atomic centers has been estimated from the crystal structure of sodium chloride by Born to be proportional to the inverse ninth power of the distance. The recent work of Lennard Jones, based on the

study of gases, gives the repulsive forces as lying between an inverse ninth power and an inverse fifteenth power, while the attractive forces lie between forces varying inversely as the fourth power and inversely as the sixth power.

With atoms and molecules of such a nature, the meaning of the term "diameter" must be modified or at least one must understand the application of the term to such a picture. Measurements of molecular diameters are made in all cases on a *very large number of individuals.* In all cases for gases they are made for individuals *oriented in all possible directions.* Finally, in the case of gases, the conditions of impact due to velocity distribution will influence the distance of approach; and one must deal with *an average value. It is possible, therefore, to couch the experimental conclusions in terms of the very simple picture of elastic spheres of a given diameter, the diameter in such a case being the statistical average distance of approach of the molecules for the average velocity.* An analysis expressed in terms of such a picture is entirely justified, as it influences the results but little, while it simplifies calculation and interpretation greatly. When such pictures are used, however, one must remember that they are conveniences and that the actual molecules may be entirely different in appearance. Even in the case of crystal analysis, the investigators find it convenient to express atomic diameters in terms of the elastic sphere.*

On the other hand, it must be clear that the values of the average diameters which are obtained for atoms and molecules from different types of investigation will not necessarily agree accurately in value, though the measurements may, in general, agree in order of magnitude. That this must be so can be clearly seen, for in a crystal two atoms are bound together by forces of electrical attraction. The average distance at which these atoms are held in equilibrium is determined by the repulsive forces as well. On the other hand, in the gaseous state, where the attractive forces may be quite different owing to the absence of closely surrounding atoms and where the velocities of agitation may be very different, the average distance of approach on an impact will not be the same as the average distance between centers in the crystal. It is also clear that the more violent the impact because of higher temperatures, the smaller will be the apparent diameter. A particular case where the results would be expected to vary from other results obtained is in the case of

* Bragg, W. L., *Phil. Mag.*, **40**, 169, 1920.

the measurement of the diameter of a molecule by the impact with electrons. The average distance of approach for an impact will be determined by the ease with which the electron is deflected from its straight-line path. It will depend on the action of the atomic field of force, on the motion of the electron. This depends on the time integral of the force and will obviously be less, the faster the electron is moving. Again, with such a minute body as the electron, the distance of approach before deflection will depend upon the portion of the atom struck. Finally, it seems probable that for electrons of a certain speed, there will be a possible interaction on the electron when its velocity in passing the atom is of the order of magnitude of the orbital velocities of electrons in the atom itself. Such effects have actually been observed. Finally, it has also been observed that electrons, moving with an extremely slow velocity in the case of certain atoms, can pass right through them without change of energy or direction (see Sec. 25). It is thus obvious that the molecular diameter, as measured by the electron, may vary through enormous ranges; and, *in comparing results of measurements on atomic or molecular diameters, one must always bear in mind that they may represent really very different things.* The conclusion is that the term "atomic or molecular diameter" has a meaning in more than order of magnitude, *only when spoken of in terms of its method of measurement.* The discussion which has preceded forms, therefore, a fitting introduction to a comparative table of molecular diameters which is given below, together with the method of measurement yielding the results.

The methods by which molecular dimensions have been obtained may be seen summarized below, as given by K. F. Herzfeld:*

I. Measurements based on the equation of state.
   1. Calculation from critical data.
   2. From volumes below the critical.
   3. Calculation from gas isotherms.
   4. Crystal structure.
      a. Spherical packing.
      b. Permutite.
      c. True dimensions.

II. Methods involving a dynamical study.
   1. In gases.
      a. Deflection of electrons.
      b. Direct measurement of free paths of atoms.
      c. Coefficient of viscosity.

* Herzfeld, K. F., *Jahrbuch der Radioaktivität und Elektronik*, **19**, 259, 1922.

2. In liquids.
   a. From Stokes' law.
   b. Viscosity in liquids.
      (1) Theory of viscosity.
      (2) Increase of viscosity in solutions.
   c. Diffusion of neutral particles.
   d. Ionic mobilities.

III. Energy methods.
   1. Heat of hydration.
   2. Ionizing potential.
   3. Heat of vaporization
   4. Melting point.

IV. Method of thin films.
   1. Determination of the number of molecules per unit area in a monomolecular layer.
   2. Optical determination of thickness of films.
   3. Electrical determination of thickness of films.

V. Optical methods.
   1. Determination of true ionic size with X-rays.
   2. Molecular refraction.

VI. Determination of the size of electronic orbits in atoms.
   1. Diamagnetic properties.
   2. Calculation from atomic models.

VII. Methods for determination of moments of inertia and electrical moments. (Such measurements give the distance between the nuclei in molecules and the distance between the apparent separation of positive and negative electricity considered as point charges necessary to produce the effects. They are not necessarily true measures of molecular diameter in the sense of the kinetic theory.)

In recent papers, J. E. Lennard Jones* gives the following values of the attractive and repulsive forces in the following gases as most successfully fitting the data. In all cases, the *attractive* force seeming to be the most suitable *is an inverse fifth power law.* For the *repulsive* forces in the following gases, the law *varies inversely* with the power of the distance indicated under the letter n for the respective gas:

GAS	n
He	9, 11, 14
Ne	11
Ar	9
Kr	10
Xe	11
H_2	11
N_2	9, 11, 14

* Lennard Jones, J. E., *Proc. Roy. Soc.*, **A-106,** 441, 463, 709, 1924; and **A-112,** 214, 230, 1926.

Radii of Molecules

Determined by Various Methods Radii Are All Given in 10^{-8} Cm.

Method	He	Ne	Ar	Kr	X	Hg	H_2	N_2	O_2
From $b = \frac{1}{8}\frac{RT_K}{p_K}$ (Van der Waals)	1.15 1.321	....	1.43 1.437	1.57	1.71	1.186	1.380	1.573	1.453
From $b = \frac{1}{15}\frac{RT_K}{p_K}$ (Wohl)	1.071	.....	1.165	1.27	1.39	0.962	1.119	1.276	1.178
*Tetrahedral packing in liquids	3.17 Temp. −271.5°	....	3.20 Temp. −189°	3.55 Temp. −146°	3.51 Temp. −102°	2.58 Temp. −39°	3.15 Temp. −258°	3.35 Temp. −202°	3.08 Temp. −227°
Gas isotherms	1.39 Temp. 0° 1.12 Temp. 293°	....	1.21 Temp. 0°	.....	.....	.....	1.16	1.49	1.325
Slow-moving electrons	1.41	1.275	2.77	.....	.....	.....	2.04	1.75	
Viscosity	.....	1.17	1.43	1.59	1.75	1.78	1.088	1.58	1.48
Molecular refraction	0.741	0.922	1.48	1.666	2.002	1.82	0.929	1.20	1.169
Diamagnetism	.....	.....	.....	.....	.....	..... 0.55	1.46	0.76	0.65
*Molecular distance from Bandspectra	.....	.....	.....	.....	.....	.....	2×0.25	....	2×0.56
Molecular distance from Chemical constants	.....	.....	.....	.....	.....	.....	2×0.26	....	2×0.77
Dipolar distance							2×0.18	2×0.97	2×1.35

Method	Cl_2	Br_2	I_2	$(CN)_2$	HF	HCl	HBr	CO	CO_2	H_2O
From $b = \frac{1}{8}\frac{RT_K}{p_K}$ (Van der Waals)	1.654	.....	....	1.893	.....	1.590	.....	2.276	1.614	1.443
From $b = \frac{1}{15}\frac{RT_K}{p_K}$ (Wohl)	1.341	.....	....	1.545	.....	1.290	.....	1.844	1.309	1.170
Tetrahedral packing in liquids	3.68 Temp. −80°	3.90 Temp. −4°	....	....	2.84 Temp. +13°	3.31 Temp. −83°	3.52 Temp. −65°	3.37 Temp. −205°	3.65 Temp. −34°	2.74 Temp. +4°
Gas isotherms										
Slow-moving electrons	.....	.....	....	......	.....	.....	.....	.....	1.83	
Viscosity	1.85	2.02	2.23	2.04	.....	.....	.....	.....	.....	1.36
Molecular refraction	1.647	1.859	....	......	.....	1.368	1.517	.....	.....	1.130
Diamagnetism	0.92									
Molecular distance from Bandspectra	.....	.....	....	......	.....	1.34	1.49	1.14		
Molecular distance from Chemical constants	.....	.....	....	......	0.924	1.276	1.419			
Dipolar distance	.....	.....	....	......	.....	.....	.....	0.94 0.025	0.0075	0.2

* Due to an error the results here are all too high by a factor of $\sqrt[3]{4}$.

APPENDIX II

FUNDAMENTAL PHYSICAL CONSTANTS*

Units: C.G.S., °C. A_n Liter, Absolute Electric

	Quantity	Value	Uncertainty
c	Velocity of light	2.9986×10^{10} cm. sec.$^{-1}$.	0.0003
G	Gravitation constant	6.66×10^{-8} cm.^{3} gram^{-1} sec.$^{-2}$	0.01
e	Electronic charge	4.774×10^{-10} es.	0.005
e	Electronic charge	[a]1.592×10^{-20} em.	
$\frac{e}{m_0}$	Electronic ratio	5.305×10^{17} es. gram^{-1}	0.010
$\frac{e}{m_0}$	Electronic ratio	[a]1.769×10^{7} emg.$^{-1}$	
F	Faraday	9.6500×10^{4} coulombs	0.0010
F	Faraday	[b]2.89365×10^{14} es.	
v_0	Volume 1 mole at 0°C.	[b]22.4115×10^{3} cm.^{3} mole^{-1}	0.002
h	Planck's constant	6.554×10^{-27} erg sec.	0.001
T_0	Ice point, absolute	273.1°C.	0.15 to −0.05
O	Atomic weight of oxygen	16.000 (by definition)	(definition)
R	Gas constant	8.315×10^{7} erg deg.$^{-1}$ moel^{-1}	
R	Gas constant	0.08206 liter atm. deg.$^{-1}$ mole^{-1}	
R	Gas constant	1.9869 cal.$_{15}$ deg.$^{-1}$ mole^{-1}	
N_a	Avogadro's number	6.061×10^{23} mole^{-1}	
N_0	Loschmidt's number	2.705×10^{19} cm.$^{-3}$ (at 0°C. A_n)	
k_0	Molecular gas constant	1.372×10^{-16} erg deg.$^{-1}$	
E_0	Translational energy of molecules, 0°C.	5.620×10^{-14} erg	
e_0	Ratio of E_0 to T_0	2.058×10^{-16} erg deg.$^{-1}$	
m_H	Mass of hydrogen atom	1.663×10^{-24} gram	
m_0	Electronic mass	8.999×10^{-28} gram	
r_1	Radius 1st Boh ring of hydrogen	0.5305×10^{-8} cm.	
$\frac{h}{e}$	Photo-electric constant	1.373×10^{-17} erg sec. es.$^{-1}$	
$\frac{h}{e}$	Photo-electric constant	4.117×10^{-15} volt sec.	
$\frac{hc}{e}$	Photo-electric constant	4.117×10^{-7} erg cm. es.$^{-1}$	
$\frac{hc}{e}$	Photo-electric constant	1.2344×10^{4} volt Å.	
β	Specific heat constant	4.778×10^{-11} sec. deg.	
σ	Stefan's constant	5.709×10^{-5} erg cm.$^{-2}$ sec.$^{-1}$ deg.$^{-4}$	
C_1	Radiation constant, first	3.703×10^{-5} erg cm^2 sec.$^{-1}$	
C_2	Radiation constant, second	1.433 cm. deg.	
w	Wien's displacement constant	0.2885 cm. deg.	
C_J	Intensity coefficient	1.301×10^{-4} erg cm.$^{-3}$ sec.$^{-1}$ deg.$^{-5}$	
ν_∞	Rydberg frequency	3.2775×10^{15} sec.$^{-1}$	
N_∞	Rydberg wave number	1.0930×10^{5} cm.$^{-1}$	
A_n	Normal atmosphere	1.013250×10^{6} dyne cm.$^{-2}$	
A.	Wave-length of red Cd line is	6438.4696 Å.	
g_s	Standard gravity	980.665 cm. sec.$^{-2}$	
Grating space in calcite		3.028 Å.	
H	Atomic weight of hydrogen	1.0077	
Liter.		1000.027 cm.^{3}	
Gram calorie (20°C.)		4.181 joule	
Gram calorie (15°C.)		4.185 joule	
Gram calorie (mean)		4.186 joule	

* These values of the fundamental constants have been taken from the International Critical Tables and will represent, therefore, the latest values. They are enclosed for the purposes of calculation for the convenience of the readers.

[a] This value is derived from the preceding one, which is the value actually accepted.

[b] Derived from volume at 0°C., $A_{45} = 22.4$; 2 liters/gram-molecule on assumption $\log_{10} \frac{A_n}{A_{45}} = 0.000\ 0214$; liter = 1000.027 cm.^{3}

APPENDIX III

For convenience in simple calculations, the following table of molecular velocities, free paths, and diameters is included. The values are not necessarily accurate and in view of Appendix I, which is much more recent, must be used with caution:

MOLECULAR VELOCITIES, MEAN FREE PATHS, AND DIAMETERS*

Gas	Velocity at 0°C.	Mean free path, L	Molecular diameter	
			η	b
	cm./sec.	cm.	cm.	cm.
Hydrogen, H_2	18.39×10^4	18.3×10^{-6}	2.47×10^{-8}	2.32×10^{-8}
Helium, He	13.11×10^4	28.5×10^{-6}	2.18×10^{-8}	2.30×10^{-8}
Nitrogen, N_2	4.93×10^4	9.44×10^{-6}	3.50×10^{-8}	3.53×10^{-8}
Oxygen, O_2	4.61×10^4	9.95×10^{-6}	3.39×10^{-8}	
Neon, Ne	5.61×10^4	19.3×10^{-6}		
Argon, A	4.13×10^4	10.0×10^{-6}	3.36×10^{-8}	2.86×10^{-8}
Krypton, Kr	2.86×10^4	9.49×10^{-6}	....	3.14×10^{-8}
Xenon, Xe	2.28×10^4	5.61×10^{-6}	....	3.42×10^{-8}
Chlorine, Cl	3.07×10^4	4.57×10^{-6}	4.96×10^{-8}	
Methane, CH_4	6.48×10^4	7.79×10^{-6}		
Ethylene, C_2H_4	4.88×10^4	5.47×10^{-6}	4.55×10^{-8}	4.68×10^{-8}
Carbon monoxide, CO	4.93×10^4	9.27×10^{-6}	3.50×10^{-8}	
Carbon dioxide, CO_2	3.92×10^4	6.29×10^{-6}	4.18×10^{-8}	3.40×10^{-8}
Ammonia, NH_3	6.28×10^4	6.95×10^{-6}		
Nitrous oxide, N_2O	3.92×10^4	6.10×10^{-6}	4.27×10^{-8}	
Nitric oxide, NO	4.76×10^4	9.06×10^{-6}	3.40×10^{-8}	
Sulph. hydrogen, H_2S	4.44×10^4	5.90×10^{-6}		
Sulph. dioxide, SO_2	3.22×10^4	4.57×10^{-6}		
Hydrochloric acid, HCl	4.30×10^4	6.86×10^{-6}		
Water, H_2O	7.08×10^4	7.22×10^{-6}	4.09×10^{-8}	

* These values are approximate and are as given by G. W. C. Kaye and T. H. Laby, "Physical and Chemical Constants," Longmans, Green & Co., London, 1911.

APPENDIX IV

For the purpose of facilitating computations involving mean free paths and problems such as ionization by collision, the following table of exponential functions is included:

Exponential Functions

x	e^x	e^{-x}	x	e^x	e^{-x}
0.0	1.0000	1.000000	5.0	148.41	0.006738
0.1	1.1052	0.904837	5.1	164.02	0.006097
0.2	1.2214	0.818731	5.2	181.27	0.005517
0.3	1.3499	0.740818	5.3	200.34	0.004992
0.4	1.4918	0.670320	5.4	221.41	0.004517
0.5	1.6487	0.606531	5.5	244.69	0.004087
0.6	1.8221	0.548812	5.6	270.43	0.003698
0.7	2.0138	0.496585	5.7	298.87	0.003346
0.8	2.2255	0.449329	5.8	330.30	0.003028
0.9	2.4596	0.406570	5.9	365.04	0.002739
1.0	2.7183	0.367879	6.0	403.43	0.002479
1.1	3.0042	0.332871	6.1	445.86	0.002243
1.2	3.3201	0.301194	6.2	492.75	0.002029
1.3	3.6693	0.272532	6.3	544.57	0.001836
1.4	4.0552	0.246597	6.4	601.85	0.001662
1.5	4.4817	0.223130	6.5	665.14	0.001503
1.6	4.9530	0.201897	6.6	735.10	0.001360
1.7	5.4739	0.182684	6.7	812.41	0.001231
1.8	6.0496	0.165299	6.8	897.85	0.001114
1.9	6.6859	0.149569	6.9	992.27	0.001008
2.0	7.3891	0.135335	7.0	1096.6	0.000912
2.1	8.1662	0.122456	7.1	1212.0	0.000825
2.2	9.0250	0.110803	7.2	1339.4	0.000747
2.3	9.9742	0.100259	7.3	1480.3	0.000676
2.4	11.023	0.090718	7.4	1636.0	0.000611
2.5	12.182	0.082085	7.5	1808.0	0.000553
2.6	13.464	0.074274	7.6	1998.2	0.000500
2.7	14.880	0.067206	7.7	2208.3	0.000453
2.8	16.445	0.060810	7.8	2440.6	0.000410
2.9	18.174	0.055023	7.9	2697.3	0.000371
3.0	20.086	0.049787	8.0	2981.0	0.000335
3.1	22.198	0.045049	8.1	3294.5	0.000304
3.2	24.533	0.040762	8.2	3641.0	0.000275
3.3	27.113	0.036883	8.3	4023.9	0.000249
3.4	29.964	0.033373	8.4	4447.1	0.000225
3.5	33.115	0.030197	8.5	4914.8	0.000203
3.6	36.598	0.027324	8.6	5431.7	0.000184
3.7	40.447	0.024724	8.7	6002.9	0.000167
3.8	44.701	0.022371	8.8	6634.2	0.000151
3.9	49.402	0.020242	8.9	7332.0	0.000136
4.0	54.598	0.018316	9.0	8103.1	0.000123
4.1	60.340	0.016573	9.1	8955.3	0.000112
4.2	66.686	0.014996	9.2	9897.1	0.000101
4.3	73.700	0.013569	9.3	10938	0.000091
4.4	81.451	0.012277	9.4	12088	0.000083
4.5	90.017	0.011109	9.5	13360	0.000075
4.6	99.484	0.010052	9.6	14765	0.000068
4.7	109.95	0.009095	9.7	16318	0.000061
4.8	121.51	0.008230	9.8	18034	0.000055
4.9	134.29	0.007447	9.9	19930	0.000050
5.0	148.41	0.006738	10.0	22026	0.000045

APPENDIX V

For the purpose of facilitating computations, a table of values of the energy distribution function e^{-x^2}, its integral, and the function $\psi(x)$ have been included:

TABLE OF VALUES FOR e^{-x^2} AND $\psi(x)$

x	e^{-x^2}	$\frac{2}{\sqrt{\pi}}\int_0^x e^{-x^2}dx$	$\psi(x)$
0.1	0.99905	0.11246	0.20066
0.2	0.96080	0.22270	0.40531
0.3	0.91393	0.32863	0.61784
0.4	0.85214	0.42839	0.84200
0.5	0.77880	0.52050	1.08132
0.6	0.69768	0.60386	1.33907
0.7	0.61263	0.67780	1.61819
0.8	0.52729	0.74210	1.92132
0.9	0.44486	0.79691	2.25072
1.0	0.36788	0.84270	2.60835
1.1	0.29820	0.88021	2.99582
1.2	0.23693	0.91031	3.41448
1.3	0.18452	0.93401	3.86538
1.4	0.14086	0.95229	4.34939
1.5	0.10540	0.96611	4.86713
1.6	0.07730	0.97635	5.41911
1.7	0.05558	0.98379	6.00570
1.8	0.03916	0.98909	6.62715
1.9	0.02705	0.99279	7.28366
2.0	0.01832	0.99532	7.97536
2.1	0.01215	0.99702	8.70234
2.2	0.00791	0.99814	9.46467
2.3	0.00504	0.99886	10.26236
2.4	0.00315	0.99931	11.09547
2.5	0.00197	0.99959	11.96402
2.6	0.00116	0.99976	12.86798
2.7	0.00068	0.99987	13.80734
2.8	0.00039	0.99992	14.78225
2.9	0.00022	0.99996	15.79255
3.0	0.00012	0.99998	16.83830

APPENDIX VI

Values of definite integrals of the form $\int u^n e^{-hmu^2} du$, from 0 to ∞ for various values of n:

$$\int_0^\infty e^{-hmu^2} du = \frac{1}{2}\sqrt{\frac{\pi}{hm}}$$

$$\int_0^\infty e^{-hmu^2} u\,du = \frac{1}{2hm}$$

$$\int_0^\infty e^{-hmu^2} u^2 du = \frac{1}{4}\sqrt{\frac{\pi}{h^3m^3}}$$

$$\int_0^\infty e^{-hmu^2} u^3 du = \frac{1}{2h^2m^2}$$

$$\int_0^\infty e^{-hmu^2} u^4 du = \frac{3}{8}\sqrt{\frac{\pi}{h^5m^5}}$$

$$\int_0^\infty e^{-hmu^2} u^5 du = \frac{1}{h^3m^3}$$

$$\int_0^\infty e^{-hmu^2} u^6 du = \frac{15}{16}\sqrt{\frac{\pi}{h^7m^7}}$$

$$\int_0^\infty e^{-hmu^2} u^7 du = \frac{3}{h^4m^4}$$

AUTHOR INDEX

Bold face type is used to indicate that the work or ideas of the author mentioned are given more than casual mention on such pages.

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